METALS AND ALLOYS

Volume 7 Number 5 May, 1936

The Magazine of Metallurgical Engineering

PRODUCTION FABRICATION
TREATMENT APPLICATION

H. W. Gillett, Editorial Director
Battelle Memorial Institute,
Columbus, Ohio

Edwin F. Cone, Editor

Richard Rimbach, Consulting Editor
1117 Wolfendale St., Pittsburgh, Pa.

EDITORIAL ADVISORY BOARD

H. A. Anderson
Western Electric Company
William Blum
Bureau of Standards
A. L. Boegehold
General Motors Corporation
P. H. Brace
Westinghouse Electric & Mfg. Co.
R. A. Bull
Consultant on Steel Castings
Junius D. Edwards
Aluminum Company of America
O. W. Ellis
Ontario Research Foundation
H. J. French
International Nickel Company, Inc.
S. L. Hoyt
A. O. Smith Corporation
J. B. Johnson
Wright Field Air Corps, War Dept.
John Johnston
United States Steel Corporation
James T. Mackenzie
American Cast Iron Pipe Company
C. A. McCune
Magnaflux Corporation
R. F. Mehl
Metals Research Laboratory, C.I.T.
W. B. Price
Scovill Manufacturing Company
Leo F. Reinartz
American Rolling Mill Company
H. A. Schwartz
Nat'l Malleable & Steel Castings Co.
F. N. Speller
National Tube Company
Jerome Strauss
Vanadium Corporation of America

Published Monthly by REINHOLD PUBLISHING CORPORATION, East Stroudsburg, Pa., U.S.A. Ralph Reinhold, President and Treasurer; H. Burton Lowe, Vice President and Secretary; Philip H. Hubbard, Vice President; Francis M. Turner, Vice President. Executive and Editorial Offices, 330 West 42nd Street, New York. Price 40 cents a copy. Annual Subscription: U. S. Possessions. $3.00. All Other Countries, $4.00. (Remit by New York Draft).

Copyright, 1936, by Reinhold Publishing Corporation. All rights reserved.

ARTICLES

Nitralloy Cylinder Barrels For Airplane Engines — Edwin F. Cone 119

The Role of Films in the Electrodeposition of Metals—I — Walter R. Meyer 123

Martensite and Austenite in Hardened Steels — Bengt Kjerrman 127

Note on Annealing Twins in Ferrite — Allan L. Tarr 130

Small Plastic Deformations in Strip Steel — Norman P. Goss 131

Magnesium Silicide in 85-15 Brass — H. S. van Klooster and J. E. Harris, Jr. 135

Notched Bar Testing—IV — S. L. Hoyt 140

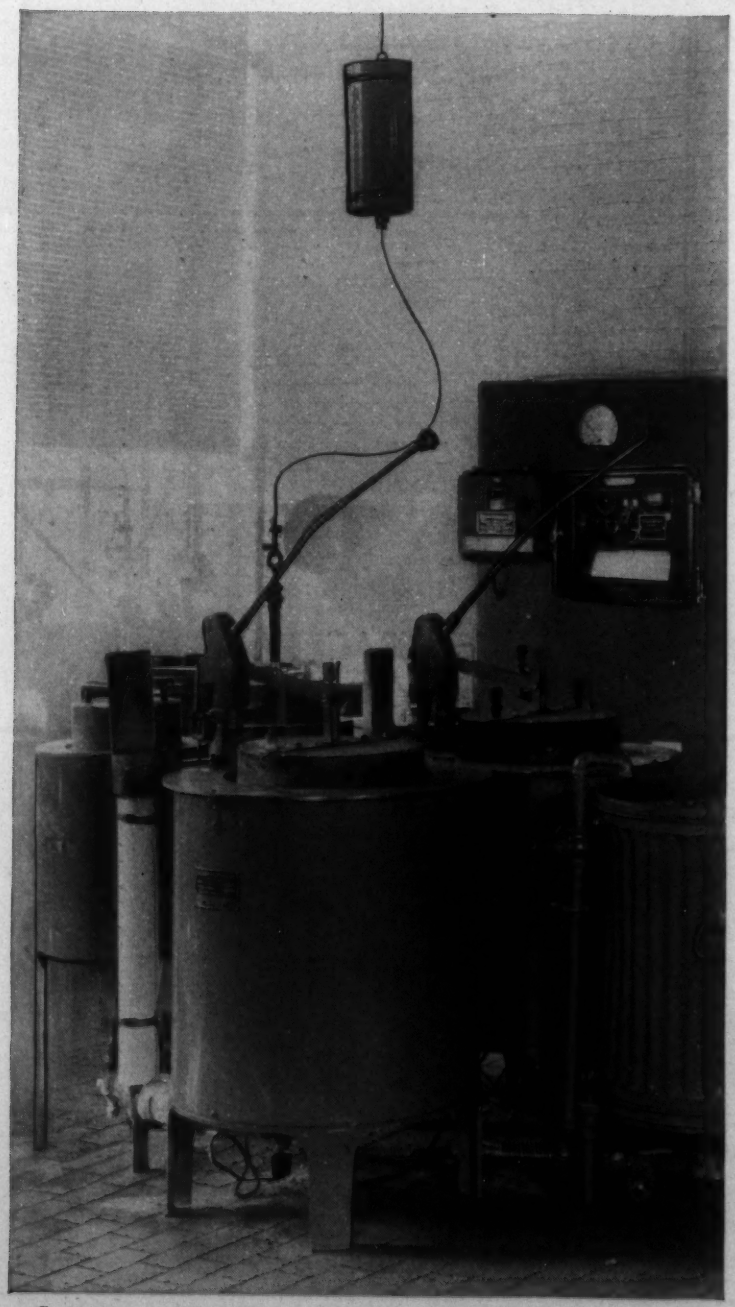
Highlights ..... A 23
Editorial Comment ..... A 25
Current News Items ..... MA 268
Manufacturers' Literature ..... MA 269
New Equipment & Materials ..... MA 271

CURRENT METALLURGICAL ABSTRACTS

Ore Concentration ..... MA 225
Ore Reduction ..... MA 226
Melting, Refining and Casting ..... MA 227
Working ..... MA 232
Heat Treatment ..... MA 233
Furnaces, Refractories and Fuels ..... MA 234
Joining ..... MA 237
Finishing ..... MA 244
Testing ..... MA 249
Metallography ..... MA 252
Properties of Metals and Alloys ..... MA 256
Effect of Temperature on Metals and Alloys ..... MA 261
Corrosion and Wear ..... MA 261
Application of Metals and Alloys ..... MA 265
General ..... MA 266

Air-hardening steel of the high-chrome, high-carbon type develops desired hardness strength and toughness at comparatively low temperature when hardened by the Triple-Control Hump Method. Here's an example from our own heat-treat.

NOW—WE MAKE TOOLS OF ANY GOOD STEELS WE WISH



Compactness, cleanliness and easy accessibility are features of this arrangement of these two Triple-Control Hump equipments in the L & N Heat-treat.

Because our own heat-treat welcomes any tool of any good steel, and hardens it successfully, we hold tool costs down to a decidedly low level.

A principal reason for the heat-treat's success in handling a wide variety of steels is that it uses the Triple-Control Hump Method of hardening. The Hump furnace takes in its stride every steel that hardens at 1850 F. or less. There's no packing, either to keep carbon in the high-chrome, high-carbon tools or to put it into the cold-rolled ones; and every tool is perfectly clean when it leaves the furnace. There is no warp; minimum change in dimensions is allowed for, and is held by the furnace's advanced control. And there are no poorly-hardened tools; for, before the heat-treater starts to quench, the steel itself has told him what structure it has, and he adjusts the depth of hardness, quench and draw accordingly. This combination of simple procedure, certain control and complete knowledge cuts heat-treating costs to the minimum.

We will be glad to help you find out to what extent Triple-Control Hump Hardening will help cut costs in your plant, as it is doing in ours and many others.

• • •

LEEDS & NORTHRUP COMPANY
4925 STENTON AVENUE PHILADELPHIA, PA.

LEEDS & NORTHRUP

Homo Tempering Furnaces

Homo Nitriding Furnaces

Triple-Control Hump Hardening Furnaces

Ho-Hump Multi-Purpose Furnaces

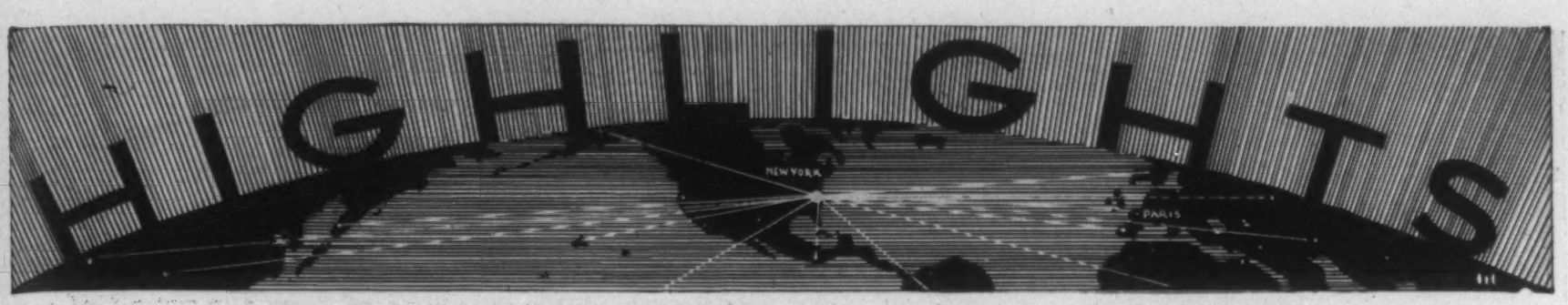
Micromax Controlling, Recording & Indicating Pyrometers

Thermotube Pyrometers

Optical Pyrometers

Precision Instruments

J-621A(4)



Written by the Abstract Section Editors and the Editorial Staff

DO YOU want to know what metallurgical engineers are saying, the world over? Look in the Current Metallurgical Abstracts. Here are some of the points covered by authors whose articles are abstracted in this issue.

Bartender Casting

Gressenich (page MA 227 L 7) discusses an aluminum piston poured from two alloys simultaneously so that the head is of one composition and the skirt of another. Which would require some skill.—H.W.G.

Deep Drawing Properties of Steels

Zimmermann claims that there is no difference in deep drawing properties whether a soft steel is rimmed or killed (page MA 229 L 7)—H.W.G.

Quantitative Blastfurnacology

Joseph (page MA 230 L 1) looks into the effect of porosity of ore on reducibility and finds some extremely interesting relationships.—C.H.H.

Radiography Has Limitations

Limitations in radiographic inspections of castings for high steam pressure are pointed out by McKinney (page MA 230 L 5).—H.W.G.

Effect of Hyrocarbon Carburizers on Abnormality

Sawamura and Imanishi (page MA 233 R 2) report that adding hydrocarbons to CO overcomes abnormality in Armco iron but not in commercial low-carbon steels.—O.E.H.

The Sun Furnace

Cohn fuses zirconia by focusing the sun's rays on it (page MA 234 L 2). One way to get arc furnace temperatures in an oxidizing atmosphere.—H.W.G.

Record the Failures

Lillicrap (page MA 237 L 2) gets tired of hearing only about the successes in welding and suggests a record of failures by which one may profit. Not a bad idea for more fields than welding.—H.W.G.

A Tough Cleaning Job

Downie (page MA 244 R 4) says that used paint and varnish cans can be cleaned by anodic treatment in soda solution. We'd call that about the toughest cleaning job yet.—H.W.G.

An M & A Non-Subscriber Misses Something

Ollard says no detailed research on use of fluorides in Cr plating is known (page MA 245 L 2). He ought to have subscribed to METALS AND ALLOYS for Perlenfein's work is abstracted in Vol. 4, June 1933, page MA 176 L 9, and that of Mueller and Vestdall, Vol. 5, June 1934, page MA 273 L 9.—H.W.G.

Grain Boundaries

Metallurgists interested in the theoretical aspects of metallic structure will be interested in some results reported by Billiter (page MA 245 L 6). He observed that when electrodeposition is carried out at very low current density, the deposit is confined to the grain boundaries of the metal upon which the deposit is made. It has long been realized by students of metal structure that the properties of the boundary zone of a grain comprising a metal structure are different in many respects from the properties of the metal comprising the remainder of the grain. This observation may offer another line of approach in studies of this kind.—H.S.R.

Impact Testing Much Discussed

The impact test is getting a lot of thought these days. "Engineering" wonders, editorially, how far notch bar impact conditions are simulated in practice (page MA 249 L 4); Burns discusses bars of various sizes (page MA 250 R 5) and Mann points out that such a range of striking velocities (or size specimen, or temperature) should be covered as to show at what point within the range of these variables brittleness ensues (page MA R 2).—H.W.G.

Where Did the Graphite Come From?

Bauer and Sieglerschmidt (page MA 250 R 6) discuss shrinkage of antimonial lead containing 0.21 per cent graphite, but neglect to state how the graphite was introduced. Their micrographs don't show any constituent one would take to be graphite. We'd think the authors should have explained this oddity.—H.W.G.

Out Goes One Mystery, In Comes Another

"Body" in steel is rapidly ceasing to be a mystery, thanks to knowledge of grain size control, which has been added to by Digges and Jordan (page MA 259 R 2), but then come Schroeder and Berk (page MA 261 R 7) with the claim that a trace of silica in NaOH accounts for the caustic embrittlement results of Parr and Straub, with no suggestion of an explanation of the mechanism involved. One boiler user remarked to us recently that if the caustic and silica idea were correct, he could not explain why all his boilers hadn't given way years ago.—H.W.G.

And Now "Semi-stainless"

Some might be pessimistic enough (or would you say mean enough?) to label all Cr steels as "semi-stainless." But now we have a classification of non-stainless, semi-stainless, and stainless Cr steels with the 8 to 10 per cent Cr steel, containing various additions of Mo, V and W, falling into the middle class as a "semi-stainless" steel and 5 per cent Cr steels designated as non-stainless.—L.J.

Cathodic Protection Marches On!

The increased interest, particularly from practical men, in the cathodic protection of pipe lines is shown in the four articles (page MA 261 R 2, R 3, R 4, and R 5). Cathodic protection is no longer an expensive theoretical possibility. It has proved to be feasible and, what is more important, economical.—V.V.K.

Hey! Handle That Carefully!

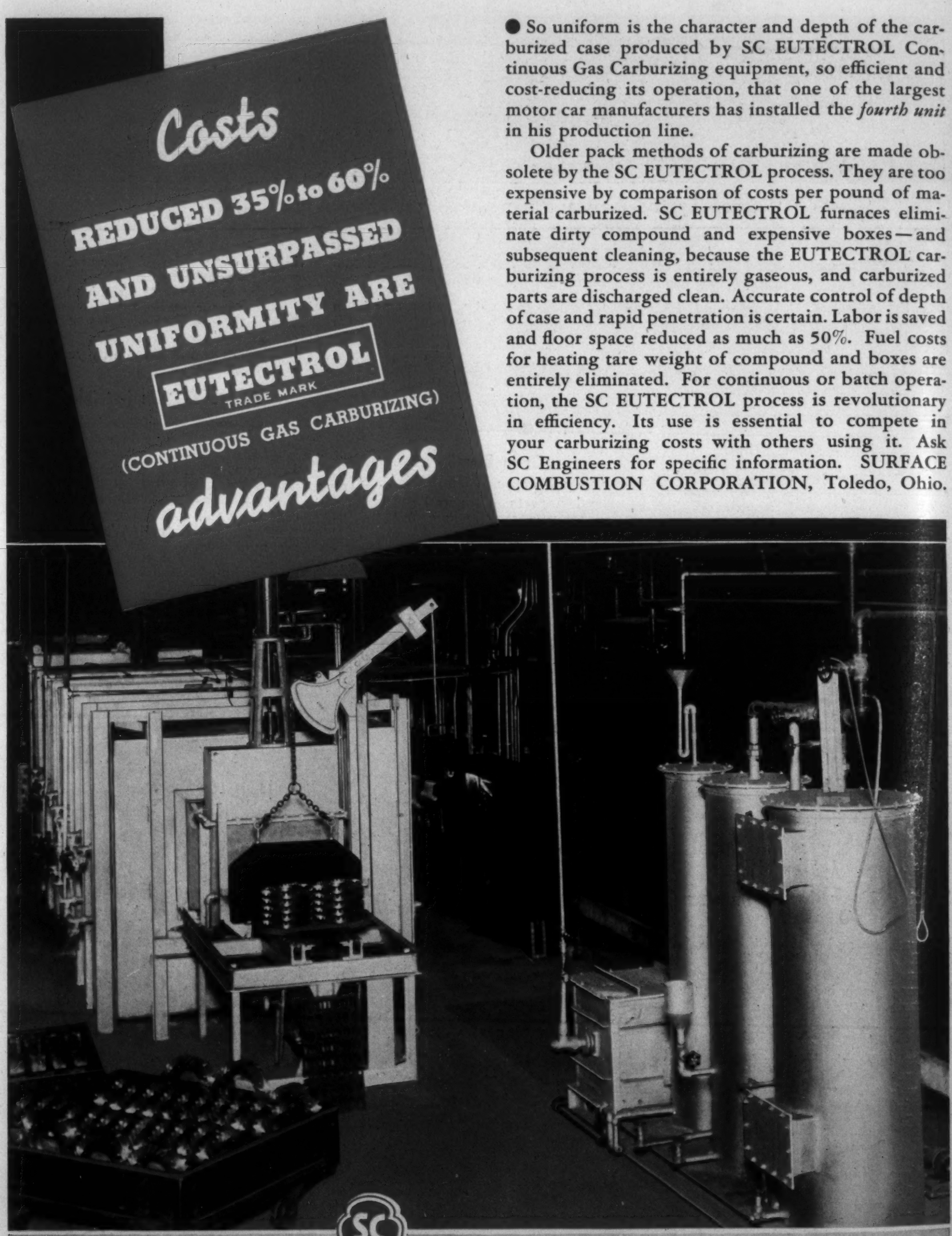
Just because that sucker-rod is steel doesn't mean that you can throw it all over the lot! Even steel can't always "take it." Shimer (page MA 261 R 6) calls attention in the case of sucker-rods to a fact that is pretty generally overlooked and that is, the importance of careful handling of materials on the job if we are to get the service we should get. This applies to the handling of all metallic materials. The mill can turn out a perfect job but it is helpless against the ignorance or carelessness of workmen and even of men in authority.—V.V.K.

A New Innovation in Bus Bars

Hollow square copper bus bars (2-6 in. rolled channels clamped together) are used extensively in the Boulder Dam power project (page MA 265 L 6). Advantages claimed over the conventional rectangular section bus bars are: higher current rating, improved ventilation, more economical use of space and higher mechanical strength.—G.L.C.

Storage Battery Plates

Schumacher and Phipps (page MA 265 L 8) point out that Pb-Ca is cheaper than Pb-Sb, and Haring and Thomas (page MA 265 L 7) indicate that it is a better battery plate alloy.—H.W.G.



● So uniform is the character and depth of the carburized case produced by SC EUTECTROL Continuous Gas Carburizing equipment, so efficient and cost-reducing its operation, that one of the largest motor car manufacturers has installed the *fourth unit* in his production line.

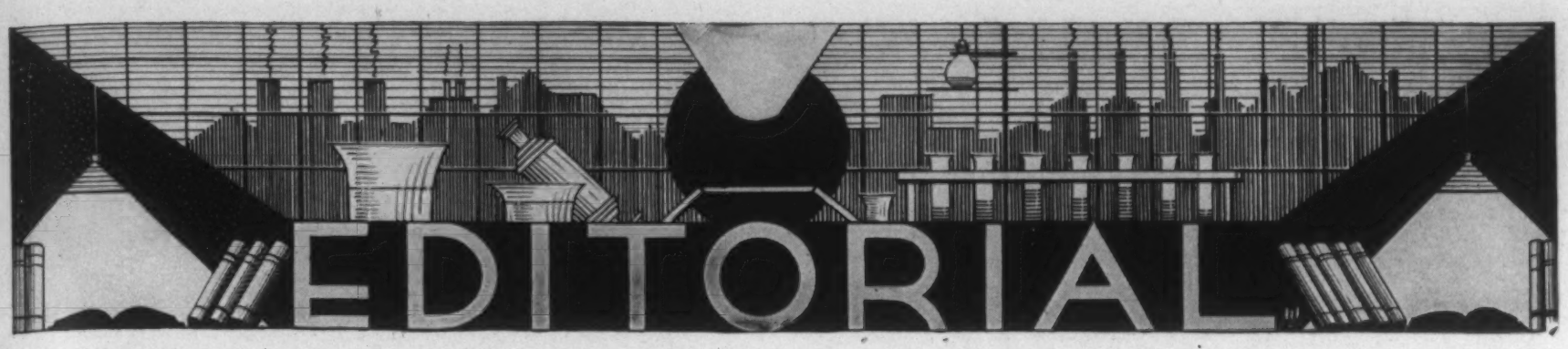
Older pack methods of carburizing are made obsolete by the SC EUTECTROL process. They are too expensive by comparison of costs per pound of material carburized. SC EUTECTROL furnaces eliminate dirty compound and expensive boxes—and subsequent cleaning, because the EUTECTROL carburizing process is entirely gaseous, and carburized parts are discharged clean. Accurate control of depth of case and rapid penetration is certain. Labor is saved and floor space reduced as much as 50%. Fuel costs for heating tare weight of compound and boxes are entirely eliminated. For continuous or batch operation, the SC EUTECTROL process is revolutionary in efficiency. Its use is essential to compete in your carburizing costs with others using it. Ask SC Engineers for specific information. SURFACE COMBUSTION CORPORATION, Toledo, Ohio.

SC

Surface Combustion

Toledo, Ohio » *Sales and Engineering Service in Principal Cities*

Builders of HARDENING, DRAWING, NORMALIZING, ANNEALING FURNACES
FOR CONTINUOUS OR BATCH OPERATION » » » ATMOSPHERE FURNACES



Who Said It?

SEVERAL of our metallurgical trade papers and journals are publishing newsy notes on timely topics, phrased to catch the attention. These often excite one's interest and create an urge to read the original and find out more about the subject, where the prosy, scientifically-phrased original itself, lacking such an introduction, would be passed over. This is all to the good, providing that the reader is directed to the original. But quite a few of these editors or columnists seem to consider it pedantic to give footnotes or other bibliographic references. In some cases we have written to the journal for enlightenment as to the source of the information and found that the reporter was unable to recall the source from which he took his data—apparently the original note is jotted down on the back of an envelope and thrown in the waste basket as soon as the copy goes to the printer.

Some of these news notes are based on exact and detailed information that is on record and could be cited, some on advertising pamphlets of the propaganda type, while some of them are based on hearsay only. We believe the reader has a right to know who said the thing cited. If that information is given, the reader can usually judge how authentic the statement is. When it is put up anonymously, the reader might properly assume that the journal which prints it is thoroughly assured that the statement is correct and sound, instead of merely reporting, as one does an abstract from a cited source, that so-and-so said thus-and-so. We are convinced that many of the news notes are not adequately checked back for correctness. We know of some that are quite incorrect, and their repetition in anonymous fashion tends to fasten the incorrect thought in the reader's mind. Thus an apparent service becomes very much of a dis-service.

When a half-baked conclusion is drawn from inadequate experimental data, or when an advertising overstatement is made, the reader of the original account can take into consideration who said it and discount it if he sees fit. If it is stated by a responsible and experienced person and supported by data, he can take it at face value. To fail to allow the reader to appraise the credibility of the statement is to fail in an important part of the reporter's duty.—H. W. G.

Propaganda

WE shall soon be in the midst of the propaganda of political conventions and elections, propaganda spread in magazines, newspapers, pamphlets, speeches and radio addresses to "my friennnds" or "my fellow-citizens." Assertions will be piled upon assertions in the hope that by reiteration they will be accepted as truth. Now and then something amusingly childish will slip past the political censor's proof reading, like the warning that the powers irregularly arrogated to the administration would be unsafe in the hands of others, which, of course, sets everyone to thinking how unsafe it is to be forced into a government by men rather than by laws, by Tugwell rather than the Supreme Court. But by and large the assertions will be fairly plausibly presented, and in the field of politics, assertions are generally unprovable one way or the other.

Everybody expects political hokum and takes it more or less as a show, not too seriously. Propaganda alleged to be based on provable facts is more insidious unless it overdoes itself, as it often does. We note an ad of the Glass Container Association of America about canned beer that amuses us. Headed "Here are the facts," it contains reference to findings of a "nationally recognized impartial testing laboratory" that "beer is better in bottles," and to a report of "certified public accountants" that "beer costs less in bottles." We have no brief for either side, our own organization is as interested in ceramics as in metallurgy, and we have no personal opinion, for we don't like beer in any form. The darned stuff smells and tastes spoiled to us whatever it has been in, but the ad makes one instinctively feel "Methinks the lady does protest too much."

Apparently held back by libel laws from alleging that canned beer spoils, it says, "But glass bottles do *not* cause cloudiness in beer and do *not* cause it to change in taste and odor while in the container." One immediately thinks of light, which glass might transmit, but would not "cause."

What we are leading up to is technical propaganda, articles that give quantitative test data and which should thus be provable if anyone cares to repeat the observations, or which give results obtained in a test run in the X.Y.Z. plant. One of the regular offenders is the type of article telling how one fuel or one furnace was replaced by another in some particular service without an economic analysis of the local fuel situation or any light on how old and decrepit or how poorly engineered the furnace was that used the replaced fuel. Such articles are the bane of an editor's existence. Some such articles record real progress, advanced engineering, new and better materials of construction, etc., and thus are informative and valuable. Even when they do, if they emanate from the maker of the furnace or the association pushing that particular fuel, we know that our readers will be prone to discount them and that we'll get cussed for publishing

(*Continued on page 129*)

—THE KEY TO *Immediate Steel*

New Steel Guide—Now Ready

For years the Ryerson Stock List has been recognized as the Key to Immediate Steel. In it you are sure to find the size, kind and quality of material you require. And the Ryerson organization with almost a century of steel service experience will cut, bend and deliver the steel and allied products on time.

There are separate books showing the local stocks at each of the ten Ryerson plants. If you have not received a copy of the 1936 spring edition, write our nearest plant. We will be glad to send it.

Partial List of Products Always In Stock:

Alloy Steels—Tool Steel	Strip Steel, Flat Wire	Hot Rolled Bars	Rails, Spikes, Etc.	Nuts, Washers, Etc.
Heat Treated Alloy Steel Bars	Mechanical Tubing	Hoops and Bands	Boiler Tubes & Fittings	Reinforcing Bars
Stainless Steel	Structurals	Plates, Sheets	Welding Rod	Babbitt Metal
Cold Finished Shafting	Channels, Angles	Tees & Zees	Rivets, Bolts	Solder, Flux, Etc.
Screw Stock				

Joseph T. Ryerson & Son, Inc., Chicago, Milwaukee, St. Louis, Cleveland, Cincinnati, Detroit, Boston, Buffalo, Philadelphia, Jersey City

RYERSON
STEEL-SERVICE

Nitralloy Cylinder Barrels

For Airplane Engines

By EDWIN F. CONE

A Douglas Super Transport Plane, Powered with Two Wright Cyclone 1,000-H.P. Engines. The nitrided cylinder barrels are used in these engines.

ADVANCES IN ENGINEERING DESIGN, involving greater demands on the strength and efficiency of the equipment, have been accompanied by the development of stronger and more durable metals or alloys to meet these conditions. This is particularly true of the airplane engine.

In the early days, a 400-horse power engine was among the most powerful then in use. Later came the development of engines ranging from 500 to 700 horse power. Today there are in use engines of 800, or more, horse power. In each step of this advance, greater power and higher rotating speed of the engine presented new problems, not only in design, but in the materials which would meet these increased requirements.

A vital part of any airplane engine is the cylinder barrel in which the pistons operate. In an 800-horse power engine unusual strength, wear resistance and other properties must be greatly intensified as compared with those of lesser power. Cylinder barrels in airplane engines are made of forged steel, properly heat treated to bring out the properties desired. Hardness to offset wear, accompanied by longer life, is an important factor.

In the earlier engines, the 400-horse power for example, an S.A.E. 1050 steel was commonly incorporated in the cylinder barrels which, after normalizing, had a Brinell hardness of about 187 to 217. In the 500 to 700 horse power engines, an S.A.E. 4140 steel—a Cr-Mo alloy—was forged into cylinder barrels. This steel, after oil quenching and drawing, had a Brinell hardness of 290 to 330 and fulfilled the demands then existing.

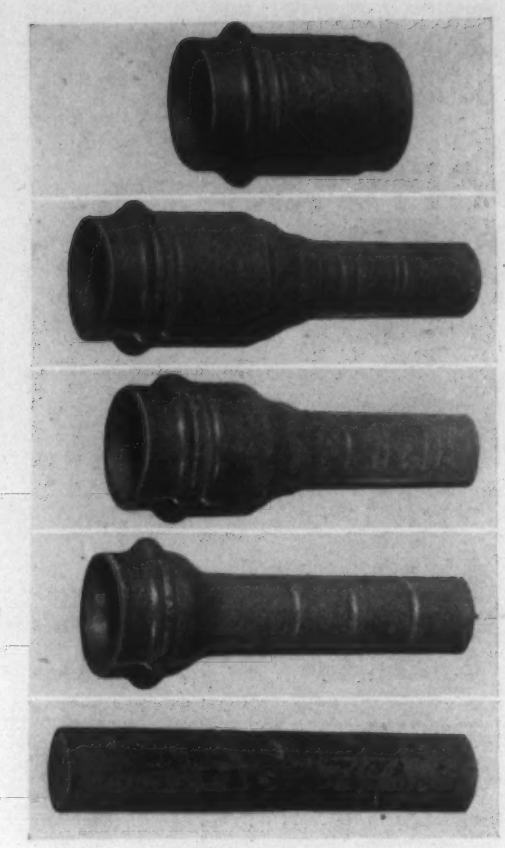
But when it came to designing a heavy duty engine of 800-horse power or over, new problems arose. It is the object of this article to briefly discuss how these problems were solved by the Wright Aeronautical Corp., Paterson, N. J., in selecting a material for cylinder barrels for its new 800-horse power heavy duty airplane engines. Besides the properties of greater strength and toughness, a higher hardness than had been possible in the earlier engines was desired. The materials previously used were not suitable.

Composition of the Nitralloy

After considerable research and experimentation it was decided that a nitralloy composition would meet the needs. A steel was developed which is a straight Nitralloy 135 (type G) modified to produce higher physical values by increasing certain alloying elements. The final composition arrived at was as follows:

	Per Cent
Carbon	0.38 to 0.45
Aluminum	1.00 to 1.30
Chromium	1.40 to 1.80
Molybdenum	0.30 to 0.45
Manganese	0.40 to 0.70
Phosphorus	0.04 max.
Sulphur	0.04 max.

An essential is that this special steel be very carefully manufactured. It is produced from selected cold stock in small electric arc furnaces of 5 to 8 tons capacity. Throughout the processing, extraordinary care and supervision are practiced. After being poured into ingots, the steel is bloomed and rolled into large rounds, 4½ to 5½ in. in diameter and 20 ft. long. Careful temperature control and inspection of the material are practiced throughout the rolling process, before these large bars are sent to the plant where the forgings are made.



Various Steps in the Production of the Forgings of Nitralloy for the Cylinder Barrels.

How the Forgings Are Made

The large majority of the nitralloy forgings for these new Wright engines have been and are being made by the Canton Drop Forging and Mfg. Co., Canton, Ohio, on a forging press of special design. This company developed a special technique for producing these cylinder barrel forgings and for handling this steel.

In the earlier days these barrels were originally bored and turned from solid billets with a waste of over 80 per cent of the steel then used, and also of time. The next step was to make them of steel tubing by extrusion. The present method is to utilize a forging machine which is said to be one of the largest in the world.

The bar of nitralloy steel, used in forging these cylinder barrels, is of the approximate diameter of the cylinder bore. The bar is upset in the first three stages shown by one of the illustrations. The fourth pass punches out the end, leaving the bar ready for the first upset in the next cylinder. In other words, the material is progressively forged and pierced from a 20-ft., 5½-in. bar of nitralloy steel with a minimum of waste. Each cylinder barrel at this stage weighs about 75 lbs. After this, the forgings are annealed and then rough turned, to specified sizes.

Although this grade of steel is not as amenable to excessive scaling, it is less plastic and harder to forge than some others. Time and temperature are important and in producing such a product, subject later to extensive inspection and machining, not only must the steel be right, but the method of forging must be as correct as possible. Other factors involve proper die construction and skilled operators. As previously stated, these forgings usually reach the aircraft engine maker, machined only on the outside, having been smooth forged inside.

It is pointed out by the Canton company that its forging process produces a highly desirable grain flow which bestows maximum strength in the flange. The special forging process employed is said to have reduced the weight of the forgings not less than 50 per cent. Forgings thus made do not require as much machining and have a uniform surface hardness.

Heat Treatment of the Forgings

The transformation of these forgings by the Wright Aeronautical Co., into finished cylinder barrels involves several important operations and exceedingly severe inspection. The first step is to subject the forgings to a heat treatment. In oil-fired furnaces batches are normalized at 1800 deg. F. and then quenched from a temperature of 1700 deg. F. after which they are drawn at 1250 deg. F. This treatment insures the desired physical properties. To facilitate the easy removal of the fairly heavy scale which forms, hydrochloric acid is put in the furnace. As a result the scale, much of it, falls easily from the forgings.

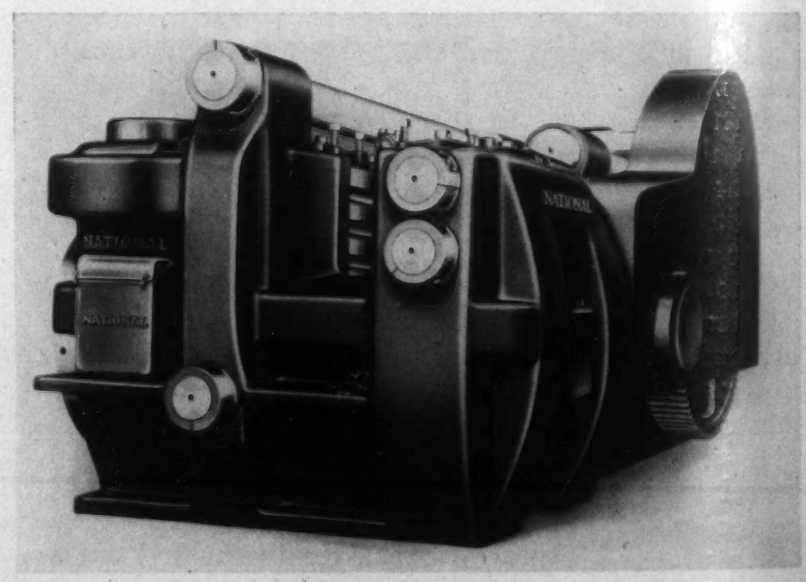
At this point the forgings are further machined all over, inside and outside, but not to final dimensions. It is the policy of the Wright company to use, as a method of nondestructive inspection, the Magnaflux process. After this machining, the barrels are subjected to this test which reveals forging cracks, inclusions or other defects which result in the rejection of the forging.

The Nitriding Operation

At this point the nitralloy forgings are nitrided. To protect the portions of the forgings which should not be hardened by nitriding, the barrels are put through an electrolytic tin plating equipment. They are, however, sealed so that the inside is not affected by the tin-plating. When they emerge from the tin-plating process, they are plated only on the outside.

For nitriding, the company has three furnaces furnished by the Electric Furnace Co. of Salem, Ohio. Each of these will nitride 48 cylinder barrels at a time. The nitriding cycle is 50 hrs. at 1,000 deg. F.

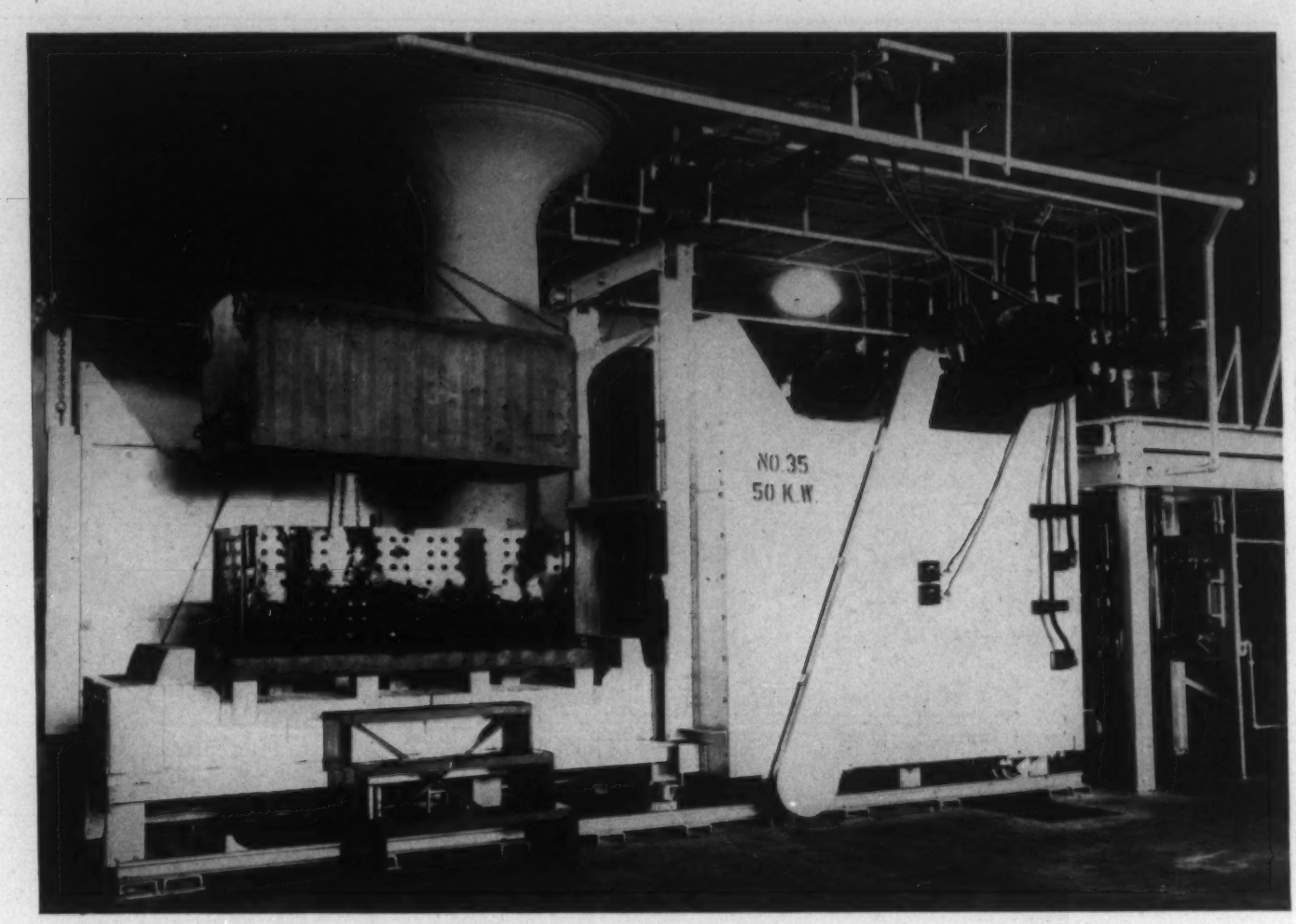
Following the nitriding operation, the cylinder barrels are machined to final dimensions, with the exception of the inside grinding operation. A feature of the machining operation is the cutting of the fins. Difficulties, usually met with in the machining of these barrels when made of steel other than nitralloy, are no more serious and the operation has been eminently successful. At this point again the Magnaflux test is brought into play for the detection of defects.



The Large Forging Machine with which the Cylinder Barrels are Produced.

The final operation on the nitralloy barrels is to grind them inside with special grinding equipment, after which they are again Magnafluxed to reveal any possible grinding cracks.

It should be emphasized that the nitriding process



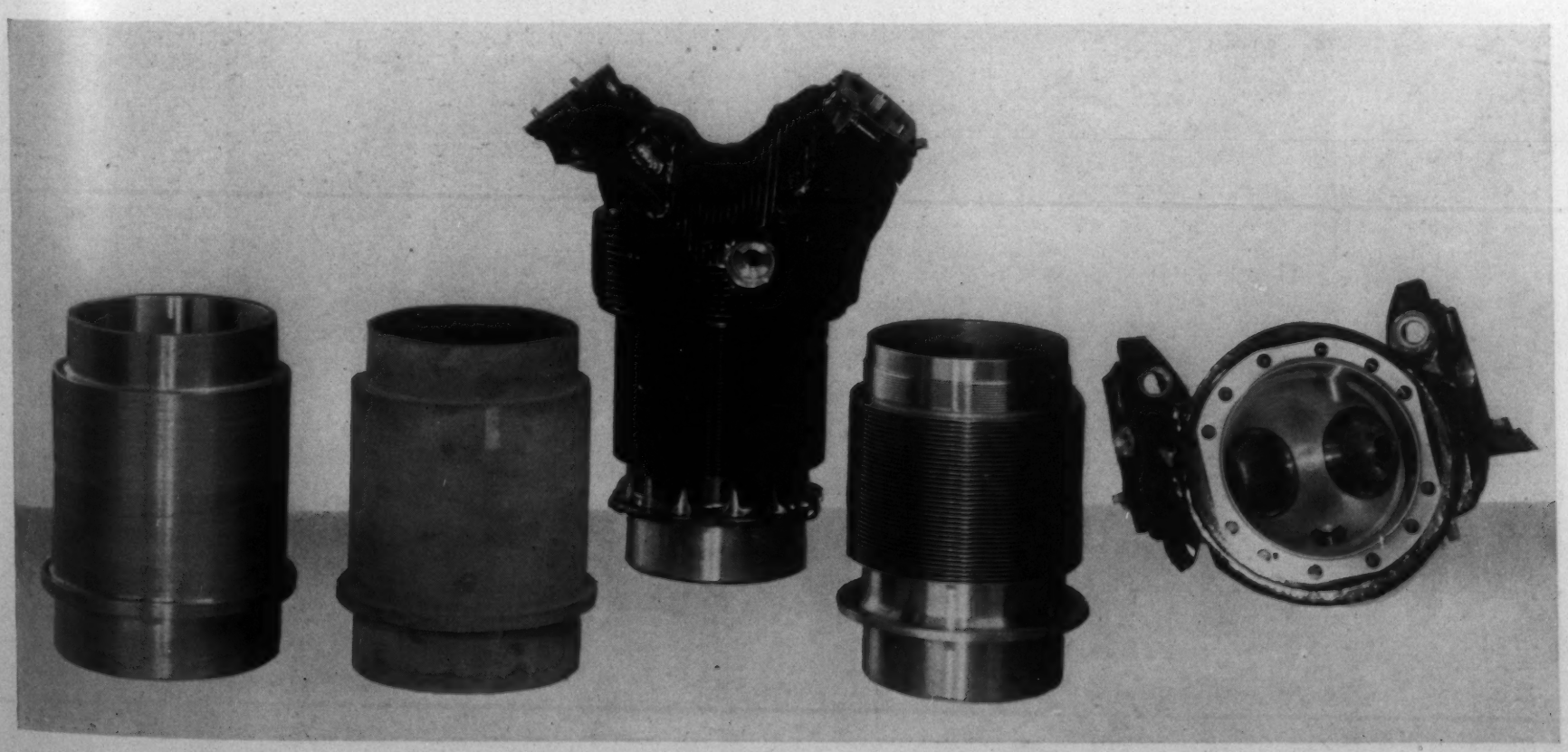
One of the Nitriding Furnaces Used in Treating a Batch of Cylinder Barrels.

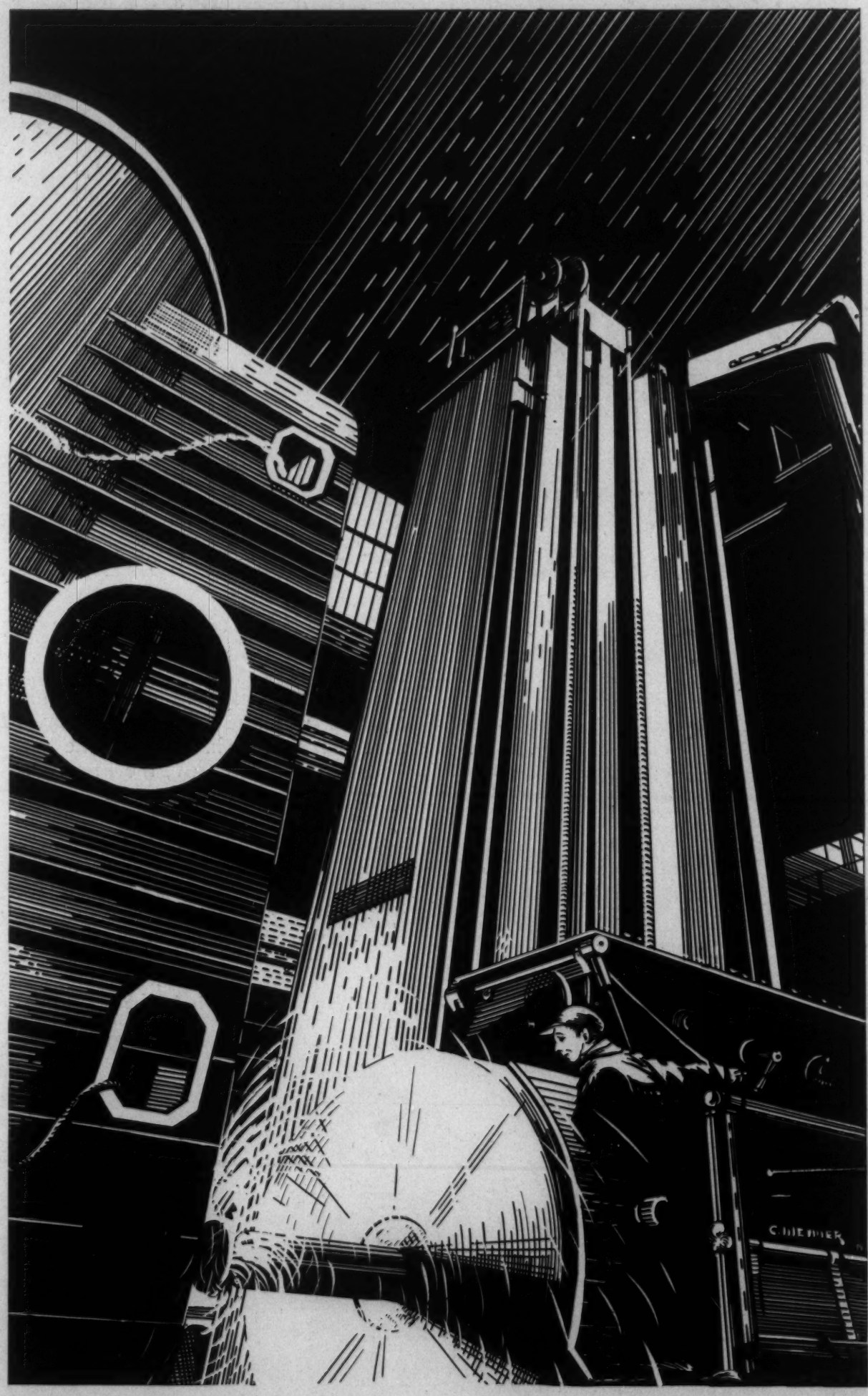
as a process will produce a hardness in this special type of steel of from 950 to 1,100 Vickers-Brinell on the finished part. The Wright Aeronautical Corp., however, uses a special nitriding cycle, already mentioned, which gives a Brinell on these cylinder barrels in the vicinity of 800 to 1,000 Vickers-Brinell. This really signifies that, while the company sacrifices somewhat the possible hardness, there is obtained a greater degree of toughness in the nitrided case which is considered to be essential.

It might also be pointed out that in the past other types of steel as cylinder barrels have been heat treated to approximately 250 Brinell, the hardness being limited because of the necessity of cutting the fins after heat treatment. By using nitralloy and hardening only the inside of the barrel, a greater hardness can be secured where it is needed in such high powered engines, without any limitations as to the delicate machine work necessary. Thus with the greatly increased hardness in the bore of the cylinder barrel due to nitriding, the life of the cylinder is decidedly enhanced because of the increased wear resistance.

From present indications, as judged by the success attending the incorporation of these nitrided cylinder barrels in heavy duty engines by the Wright Aeronautical Corp., it is not unlikely that this may develop into one of the largest applications of nitralloy.

The Forged Cylinder Barrel Before and After Machining and How It is Assembled.





Drawing by Charles Perry Weimer

A MACHINING OPERATION

The Role of Films in the Electrodeposition of Metals—I

A Correlated Abstract

By WALTER R. MEYER

Electrochemist, General Electric Co., Bridgeport, Conn.

THE PHYSICAL-METALLURGICAL relationships of the basis metal and the role of films on the metal prior to electrodeposition have been studied extensively during the past five years. The advent of chromium plating and the use of heavier electrodeposits,[1] as demanded by the automobile industry for outdoor exposure, has forced the electroplater into new difficulties of exfoliation, "throwing power," and distribution of thickness, the solving of which has lead to critical considerations of the surface condition of the metal to be plated and particularly that of film formation.

In recognition of the vastness of the work published on surface chemistry, this abstract has of necessity been limited to the film relationships with the problems of adhesion of the electrodeposit, its crystalline structure, and the distribution of the coating. Some observations on film formation upon the electrodeposit itself, particularly in regard to corrosion resistance, have been included. A fairly complete survey of all relevant papers, published within the last ten years, has been made and a few outstanding ones published previous to this, were consulted. The semi-technical literature has been culled for observations on existing problems, even though the true explanation of the phenomena concerned was not apparent to the particular authors.

This correlated abstract will be divided into three sections: The first, devoted to the formation and structure of four classes of films—namely, preferential-solution films, deposited films, passive films, and polishing films; the second, a description of the effects of these films on the adhesion, crystal structure, and coverage of the electrodeposit; and the third, a review of some films prepared artificially upon the electrodeposit itself and in some cases upon the unplated metal.

Preferential-Solution Films

Preferential-solution films are formed by the non-uniform action of the cleaning and pickling solutions used in preparing the work for plating, upon the different components of alloys which are to be plated. In the pickling of cast iron or steel, either in a non-electric or cathodic pickle, smuts of carbon or carbides have proved to be particularly troublesome in causing non-adherence of the plated coating. Hogaboom[2] has called attention to 0.04 per cent carbon, cold-rolled steel which may have a skin containing as much as 0.80 per cent carbon. Anodic pickling[3, 4] in strong sulphuric acid solutions, as used in the Madsenell process[5] or the Hanson-Van Winkle-Munning bright dip,[6] successfully removes the carbon smut, leaving a clean white surface to insure adherence of the plated coating.

In the electroplating of aluminum alloys containing copper and silicon, preferential-solution films are commonly encountered, necessitating the use of a mixture of nitric and hydrofluoric acids[7] for their removal. Copper in zinc-base die castings, lead in brass, and antimony in lead[8] are frequently the cause of smutty film formation in the cleaning and pickling of the respective alloys (Figs. 1 and 2). Preferential-solution films are invariably non-adherent and if non-conductors of electricity will lead to incomplete coverage of the plate. In most cases, however, they conduct sufficiently to allow deposition of the plate, which will ultimately blister or peel away from the basis metal because of the low tensile strength of the film in relationship to the strains[9, 10, 11] in the electrodeposit.

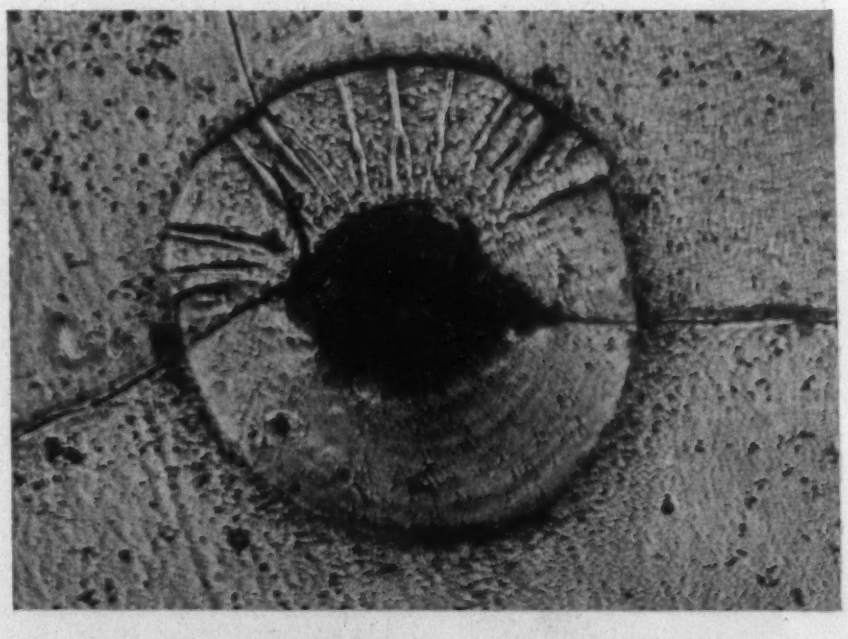


Fig. 1 Pit in Nickel Plating From Film With Low Hydrogen Over-Voltage.
Notice the cracks in the nickel plate radiating from the pit. The concentric rings are due to the successive forming and breaking of bubbles of hydrogen. After W. R. Meyer.[8]

Deposited Films

The influence of grease and dirt films[12] on the adhesion of plated coatings is too well known to need further consideration here. Deposited films such as colloids, smuts plated in the cleaning processes, and films formed by differences in solution pressures have been subjected to much study during the last few years.

Absorbed films at metallic cathodes usually have a small effect on the potential at low current densities, but the effect may increase at larger currents. Newbery[13] found that colloids such as dextrin, gelatin and gum arabic increased the overvoltage at lead, platinum and mercury cathodes. P. A. Jacquet[14] found that certain hydrophilic colloids (proteins and their disintegration products) form absorption films on metal surfaces such as copper, nickel, iron, and platinum, which films materially reduce the adhesion of electrolytic deposits to such surfaces (Table 1). Hogaboom[15] has pointed out that in cathodic cleaning, deposition of colloids may take place, resulting in pitting or roughening of the subsequent electrodeposit.

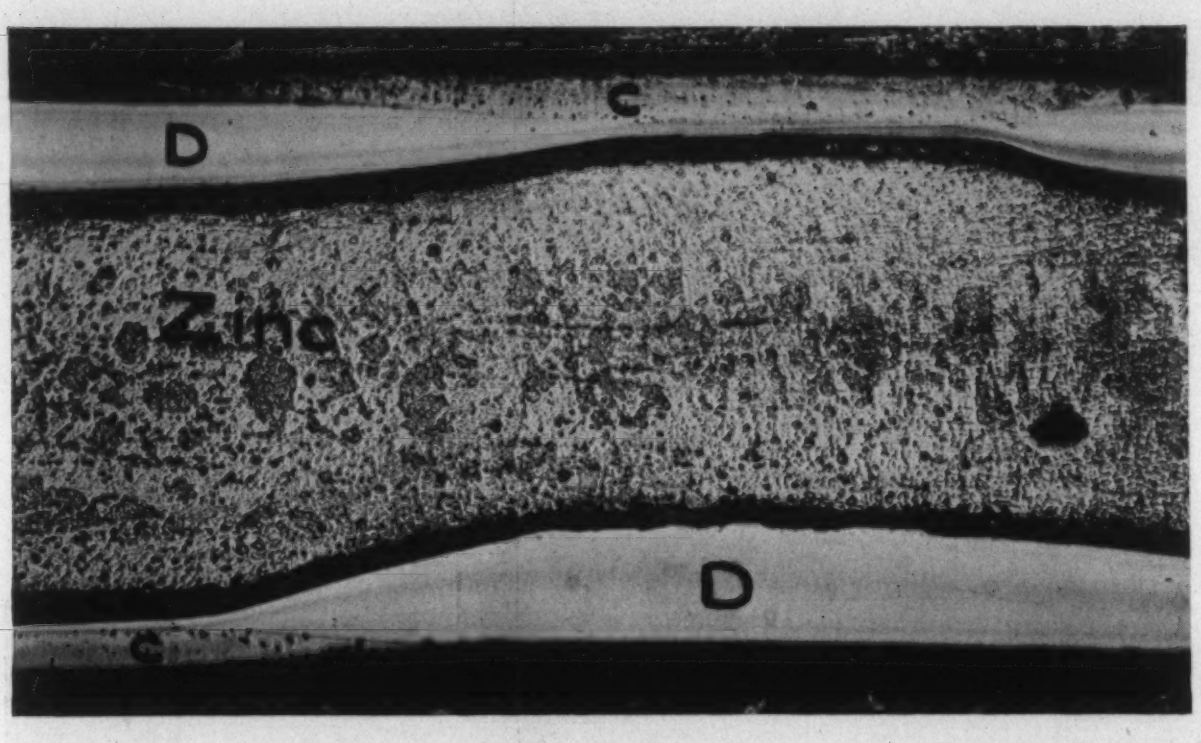


Fig. 2. Diffusion of Copper Plate Into Zinc Showing Variability Due To Films Between the Copper and the Zinc.

The zones marked "D" are diffusion zones of copper and zinc formed by heating the plate to 140 deg. C. for 18 hrs. The sections marked "C" are undiffused copper plate. After W. R. Meyer.

It is common knowledge that films, deposited by differences in electrolytic solution pressure, are relatively poorly adherent in comparison with those formed by the electric current. Immersion-film formation has been used, however, in the electroplating of aluminum alloys because of the rapidity with which aluminum oxidizes after being etched. Ledin[16] employed cadmium, Ryan[17] used mercury, Canac[18] used iron, and Work[19] recommended iron, nickel or manganese, depending upon the alloy to be plated. Tsuboi,[20] in a study of the fibrous structure of lead and cadmium deposited by immersion of zinc in their respective solutions, found that the majority of the lead crystals had one of the (111) planes of the cubic crystals, nearly parallel to the flat surfaces of the deposit, and in the cadmium deposits the (0001) plane of the hexagonal crystal is nearly parallel to the flat surfaces of the specimen.

Table 1.—Adhesion of Electrodeposits to Basis Metal Covered with a Colloid Film. Protein Colloids Compared with Hydroxyl Colloids.—P. Jacquet[14]

Colloid	Minimum concentration (mg./L.) necessary to produce non-adherent deposits
Serum albumin *	4
Casein peptone	15
Sodium caseinate	20
Gelatin	25
Ovalbumin	30
Fibrin peptone	60
Gum arabic	x (> 10.000)
Gum tragacanth	x (> 10.000)
Dextrine	x (> 10.000)

* This albumin was prepared by Mr. Piettre from ox blood using the acetone method.

In an earlier study Tsuboi[21] found that silver, deposited from silver nitrate on copper, has a fibrous structure, the crystals having a definite orientation to the plane of the copper upon which they were deposited. W. Sack,[22] in the commercial silver plating of brass, experienced the difficulty of peeled coatings whenever a steel wheel was used to brush the brass previous to plating the silver. The difficulty was attributed to the precipitation of silver by electrolytic solution pressure of the film of iron remaining on the brass after it had been brushed with the iron brush.

After a cathodic electrocleaner has been in use for some time, a film of various metals will begin to deposit[23] which is structurally weak and poorly adherent to the basis metal. The adhesion of the plated coating will consequently be poor. C. J. Reed[24] studied cathodic films on lead in borax solutions and F. Haber[25] described the formation of metallic dust on tin and lead cathodes with the resultant poor adhesion. A. W. Hothersall[26] quantitatively measured the effects of plated films in electrocleaning solutions and found they materially lowered the force of adhesion. W. R. Meyer[27] analyzed some plated smuts in commercial cleaning and found tin, zinc, lead, iron, and copper. Reversal of the electric current, making the work the anode, removed the tin, lead and zinc, but the iron and copper were not removed. The effects of cyanide, soap, and insoluble salt films have all been discussed in the literature but sufficient quantitative data have not been accumulated to warrant further discussion here.

Passive Films

The expression "passive films" is used in a general sense to indicate naturally or artificially formed films on metals, the thickness of the films not being greater than several hundred Ängstrom units. Scale coatings, such as rust or magnetic scale on iron, are not considered in the category of passive films. Passivity plays an important part in the electrodeposition of metals both at the anode and the cathode. E. S. Hedges[28] has considered at length the role of passivity in anodic processes with particular reference to the effects of temperature, time, and current density. Two valuable tools in the study of passivity have been the electron diffraction camera[29] and optical methods as employed by Leif Tronstad[30] and his co-workers.

Faraday,[31] as early as 1836, recognized the nature of passivity of iron imparted by concentrated nitric acid to be an oxide film of a continuous nature. Ralph Snowden,[32] in 1905, attributed the peeling of nickel

films deposited upon nickel to the invisible oxide which coated the first deposit. Reduction by electrolysis in 3*N* HCl was recommended for the removal of the film. Similar problems are met in the plating of stainless steel[33, 34] and "duplex" plating on zinc.[35] Passive films influence the interfacial surface tension between liquid and metal[36] and may alter the "throwing power" of solutions, as, for example, was found by Korpium and Vogel[37] in a study of chromium plating on bright nickel.

U. R. Evans,[38] in a study of obstructive films in anodic processes, classifies the products of the anodic attack in three groups: (a). Soluble products giving only concentration polarization; (b). insoluble but porous and non-adherent products which increase concentration polarization by slow diffusion; (c). adherent and insoluble films having pronounced effects. The reaction product may often stop the reaction, such as the use of a silver anode in HBr solution.[39] If the product is a non-conductor of electricity but contains pores filled with oxygen, no current will pass. If the current is reversed, free electrons can pass from metal across the plate resulting in what is called "valve action."[40] The adhesion of a substance to an interface in the final state of equilibrium will be determined by the values of the interfacial energies between the three materials concerned; namely, metal, solution, and anodic product. This applies to the final stage of equilibrium, and in dealing with irreversible changes other factors may be very important in determining adhesion, for example, the exact position where the film is formed.[41] Müller and Konopicky,[42] from electrometric investigations with copper, nickel, iron, and chromium, suggested that the passivity of these metals in certain acid solutions was due to the formation of a poorly conducting film of metal salt on the anode. Such a film would cause progressive diminution of the available surface of the anode with a subsequent increase in the current density at the still active surface. McCulloch[43] pointed out that the rate of dissolving, and not the limiting solubility, was important in determining anodic passivity.

W. H. J. Vernon[44] made an exhaustive study of film formation on copper, zinc, brass, aluminum, lead, and iron by gravimetric methods and found, for example, that, for copper, the minimum thickness of film necessary for protection was such that the unit lattice of the oxide is completed for the entire surface. Vernon later reported[45] that dust particles suspended in the air exert a pronounced effect in preventing the formation of a continuous oxide film on copper. L. Tronstad,[46] using reflected polarized light, added more evidence to the belief that passivity is caused by oxide films. Studying alternate activation and passivation it was found that the optical constants did not return to the same value as before passivation, indicating that the passive film was not totally destroyed upon activation. H. Freundlich and collaborators,[47] using optical methods, showed that the change in properties of the passive film occurred before it reached visible dimensions. The film formation is rapid up to 10 Ängstrom units and the normal oxide film (15-30 A.) cannot be considered to be mono-molecular (in the sense of Langmuir) at low temperatures.

U. R. Evans[48] showed the presence of invisible oxide films on iron by the non-reactance with reagents such as copper sulphate and silver nitrate. Evans and Stockdale[49] succeeded in isolating the surface oxides of metals by anodic undermining. The thin and highly protective films were the most difficult to remove. The oxide on heat-tinted nickel was sharply divided from the metal, but on iron and copper there was interlocking. Using the new tool of electron diffraction, W. L. Bragg and J. A. Darbyshire[50] detected copper oxide with cuprite structure on copper, NiO with a rock salt structure on nickel, lead dioxide with a rutile structure on lead, and stannic oxide, also with a rutile structure, on tin.

The oxide film formation on copper was studied by F. H. Constable,[51] W. Feitknecht,[52] and Mehl, McCandless and Rhines.[53] The last named authors found that cuprous oxide forms on a single crystal of copper without change of orientation until the thickness reaches at least 5×10^5 A. Kutzelnigg[54] studied the anodic passivation of copper in mixtures of potassium nitrate and sulphuric acid. An interesting case of practical film formation was reported by Finch, Quarrel, and Wilman,[55] who discovered that, when a polished copper surface was cleaned in trichlorethylene vapor, it lost the power of absorbing crystalline metal films, owing to the formation of an invisible layer of crystalline cuprous chloride in (111) orientation.

Shimadzu[56] by sending K radiations of iron to the surface of lead contaminated by oxide found that the oxide had penetrated deeply, to from 500 to 2000 A. W. J. Müller and W. Machu[57] reported that lead dissolves anodically in sulphuric acid at —0.3 volts in the divalent condition to form lead sulphate, and at 2 volts in the tetravalent state to form lead peroxide.

A thin protective oxide film on aluminum has long been believed to form readily. U. R. Evans[58] succeeded in isolating the natural film as flakes. H. Sutton and J. W. Willstrop[59] isolated the oxide formed from the anodic oxidation of aluminum, and obtained films varying in thickness from 300 A. to 20,000 A. Tehnicheskoi,[60] from X-ray analyses of films formed by anodizing aluminum in oxalic acid baths, reported the oxide to be gamma Al_2O_3 of a crystalloidal nature, whereas the films formed in sulphuric acid baths were microcrystalline with a grain size of 100 A. L. Tronstad and T. Höverstad,[61] employing optical methods, determined the thickness of artificial oxide films on aluminum to be 300 A. and the natural film to be 110-130 A.

Using the electron rays to investigate the surface films on aluminum, A. Steinheil[62] determined the oxide to be face-centered cubic with a = 5.35 A. The oxide film grew rapidly in the first two days to 300 A. and then required a month to reach a thickness of 400 A.

The anodic passivation of gold in chlorides and sulphates has been determined by W. Shutt and A. Walton[63] to be due to a gold peroxide film continuous with the lattice structure of the metal.

The passive films on nickel, as previously mentioned, have proved to be very troublesome in practical electroplating. The oxide film is difficult to remove, requiring in some cases electrolytic etching or pickling for its removal to secure adherent coatings upon the nickel. J. Steiner and L. Kahlenberg[64] found that nickel would passify in 52 to 53 per cent nitric acid whereas 58 per cent acid was required for iron under the same conditions. Five per cent of nickel in iron allowed passivation of the iron-nickel alloy as readily as pure nickel itself. W. Müller, H. Cameron, and W. Machu[65] found that the time for passivation of new nickel was very short and that immersion of clean nickel into sodium sulphate solutions renders the nickel instantaneously passive. The oxide was found to be very stable. G. D. Preston,[66] using electron diffraction methods, determined the oxide on nickel to be NiO with a rock salt type of lattice.

Finch and Quarrell[67] showed that the product of the oxidation of zinc in air within the first few hours is an oxide film, which is basically pseudomorphic with the underlying zinc and is highly oriented in that it forms a continuation of the zinc lattice.

The influence of the passive film on chromium in respect to its tarnish resistance is well known. The film is very thin and rapidly self-healing. F. N. Speller[68] regards the stainless qualities of nickel-chromium alloy steels to be due in a great measure to the stable, relatively non-permeable oxide films of the alloying constituents. Adherent electrodeposits are obtained with difficulty upon alloy steels because of the difficulty in securing a film-free surface. E. Müller[69] reports that electrodeposited chromium is passive at 0 deg. C. to *N* solutions of HCl, HBr, $HClO_4$, and HNO_3. The first four acids make the chromium active when warmed, but perchloric and phosphoric acids have no effect at 100 deg. C.

Extensive potentiometric, optical, and diffraction studies have been made of passive films on iron. Shutt and Walton[70] found that iron formed a film on standing several minutes in neutral potassium sulphate solutions and that treatment with alkali or even distilled water accelerated the film formation. L. Tronstad and T. Höverstäd[71] from optical experimentation calculated the mean thickness of the natural passive film on pure iron to be about 20 A. Anodic passivation gave a film 50-70 A. thick. Tronstad and Borgman[72] found that natural oxide films were strengthened when immersed in nitric or chromic acids, and reached 100 A. from the nitric acid treatment. The thickness of the oxide on stainless steel was calculated to be 10 A. Using the electron diffraction camera, G. P. Thomson[73] determined the oxide that forms on iron when immersed in concentrated nitric acid to be a mixture of ferric oxide and Fe_3O_4.

Both the thin and thick oxide films have significant effects on the manipulative technique and the structure of the electrodeposit. Hothersall[74] has shown that unremoved passive films will cause non-adherence and, indeed, common experience is well aware of this difficulty. In connection with the examination of polished metal surfaces, Tronstad[75] discovered that rouge had a tendency to give off oxygen to the metal which was being polished, and he suggested that, because of its high heat of formation, aluminum oxide be used for polishing to avoid this difficulty. The anode and cathode resistances and efficiencies, and the extent of coverage of the basis metal by the electrodeposit are strongly influenced by film formation. The influence of film removal on the structural relationships between the deposit and the basis metal will be considered later.

(To be continued)

Bibliography

[1]Wm. Blum, P. Strausser and A. Brenner. *Journal of Research,* National Bureau of Standards, Vol. 13, 1934, page 331.
[2]G. B. Hogaboom. *Monthly Review,* American Electroplaters' Society, Vol. 21, 1934, page 7.
[3]B. H. Thomas. *Proceedings,* Institution of Automobile Engineers (London), Vol. 14, 1920. page 603.
[4]J. P. McLare. *Transactions,* Faraday Society, Vol. 20, 1924, page 87.
[5]F. M. Dorsey. Madsenell Process. *Industrial and Engineering Chemistry,* Vol. 19, 1927, page 1219; Vol. 20, 1928, page 1094. Patent No. 1,564,710.
[6]Patent No. 1,865,470.
[7]"Electroplating Aluminum." Aluminum Co. of America, 1930, page 16.
[8]W. R. Meyer and Clarence Helmle. *Proceedings,* Annual Convention of American Electroplaters' Society, June 1935, page 129.
[9]E. A. Vuilleumier. *Transactions,* American Electrochemical Society, Vol. 42, 1922, page 99.
[10]C. Marie and N. Thon. *Journal de Chimie Physique,* Vol. 29, 1932, page 11.
[11]V. Kohlschütter and H. Schödl. *Helvetica chimica acta,* Vol. 5, 1922, pages 490, 593.
[12]C. Marie and N. Thon. *Journal de Chimie Physique,* Vol. 29, 1932, page 569.
[13]E. Newbery. *Journal,* Chemical Society of London, Vol. 105, part 2, 1914, page 2419.
[14]P. Jacquet. *Comptes Rendus,* Vol. 196, 1933, page 921; *Transactions,* American Electrochemical Society, Vol. 66, 1934, page 393.
[15]G. B. Hogaboom. *Monthly Review,* American Electroplaters' Society, Vol. 19, 1932, page 30.
[16]Ledin. *Metal Industry,* (N. Y.), Vol. 20, 1922, page 351.
[17]Ryan. British Patent No. 12,390 of 1899.
[18]J. Canac. *Comptes Rendus,* Vol. 158, 1914, page 119.
[19]H. Work. *Transactions,* American Electrochemical Society, Vol. 53, 1928, page 361.
[20]Shogo Tsuboi. *Memoirs,* College of Science, Kyoto Imperial University, Vol. 12, 1929, page 209.
[21]Shogo Tsuboi. *Memoirs,* College of Science, Kyoto Imperial University, Vol. 11, 1928, page 271.
[22]W. Sack. *Licht und Lampe,* Vol. 18, 1929, page 1181.
[23]W. E. Hughes. *Metal Industry* (London), Vol. 33, 1928, page 173; Blum and Hogaboom, Principles of Electroplating and Electroforming, McGraw-Hill Book Co., 1930 Edition, page 144.
[24]C. J. Reed. *Journal,* Franklin Institute, April, 1895.
[25]F. Haber. *Transactions,* American Electrochemical Society, Vol. 2, 1902, page 189.
[26]A. W. Hothersall. *Journal,* Electroplaters' and Depositors' Technical Society, Vol. 7, 1932, page 115.
[27]W. R. Meyer, *Monthly Review,* American Electroplaters' Society, Vol. 21, 1934, page 40.
[28]E. S. Hedges. "Protective Films on Metals," Chapman and Hall, Ltd., London. 1932.
[29]G. P. Thomson. *Proceedings,* Royal Society, Vol. 119A, 1928, page 652. See No. 55.
[30]Leif Tronstad. *Transactions,* Faraday Society, Vol. 31, 1935, page 1151.
[31]M. Faraday. *Philosophical Magazine,* Vol. 9, 1836, page 53.
[32]Ralph Snowden. *Transactions,* American Electrochemical Society, Vol. 7, 1905, page 301.
[33]J. Hoefer. *Monthly Review,* American Electroplaters' Society, Vol. 20. 1933, page 22.
[34]*Oberflächentechnik,* Vol. 11, 1934, page 144.
[35]E. A. Anderson. *Monthly Review,* American Electroplaters' Society, Vol. 22, 1935, page 27.
[36]G. Tammann and F. Arntz. *Zeitschrift für anorganische und allgemeine chemie,* Vol. 192, 1930. page 45.
[37]J. Korpium and E. Vogel. *Oberflächentechnik,* Vol. 10, 1933, page 243.
[38]U. R. Evans. *Transactions,* Faraday Society, Vol. 19, 1923, page 789.
[39]G. Schultze. *Annalen der Physik,* Vol. 26, 1908, page 372.
[40]G. Schultze. *Annalen der Physik,* Vol. 22, 1907, page 543; *Transactions,* Faraday Society, Vol. 9, 1914, page 266.
[41]U. R. Evans. *Transactions,* Faraday Society, Vol. 18, 1922, page 1.
[42]Wolf J. Müller and K. Konopicky. *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften,* Vol. 48, 1927, page 711; W. J. Müller. *Monatsheft,* Vol. 48, 1927, page 559.
[43]Leon McCulloch. *Transactions,* American Electrochemical Society, Vol. 56, 1929, page 325.
[44]W. H. J. Vernon. *Journal,* Chemical Society of London, Vol. 128, part 2, 1926, page 2273.
[45]W. H. J. Vernon. *Transactions,* American Electrochemical Society, Vol. 64, 1933, page 31.
[46]Leif Tronstad. Transactions, Faraday Society, Vol. 29, 1933, page 502; *Nature,* Vol. 124, 1929, page 373.
[47]Freundlich, Patscheke and Zocher. *Zeitschrift für physikalische Chemie,* Vol. 128, 1927, page 321; Vol. 130, 1927, page 289.
[48]U. R. Evans. *Journal,* Chemical Society of London, Vol. 129, part 1, 1927, page 1020; Vol. 127, 1925, page 2484.
[49]U. R. Evans and J. Stockdale. *Journal,* Chemical Society of London, Vol. 131, 1929, page 2651.
[50]W. L. Bragg and J. A. Darbyshire. *Transactions,* Faraday Society, Vol. 28, 1932, page 522; J. A. Darbyshire, *Transactions,* Faraday Society, Vol. 27, 1931, page 675.
[51]F. H. Constable. *Nature,* Vol. 123, 1929, page 569; *Proceedings,* Royal Society, Vol. 125A, 1929, page 630.
[52]W. Feitknecht. *Zeitschrift für Elektrochemie,* Vol. 35, 1929, page 142.
[53]R. F. Mehl, E. L. McCandless and F. N. Rhines. *Nature,* Vol. 134, 1934, page 1009.
[54]A. Kutzelnigg. *Zeitschrift für Elektrochemie,* Vol. 39, 1933, page 67.
[55]Finch, Quarrell and Wilman. *Transactions,* Faraday Society, Vol. 31, 1935, page 1151.
[56]Shinichi Shimadzu. *Memoirs,* College of Science, Kyoto Imperial University, Series A, Vol. 17, 1934, page 79.
[57]W. J. Müller and W. Machu. *Monatsheft,* Vol. 63, 1933, page 347.
[58]U. R. Evans. *Journal,* Chemical Society of London, Vol. 129, part 1, 1927, page 1020.
[59]H. Sutton and J. W. Willstrop. *Journal, Institute of Metals,* Vol. 38, 1927, page 259. *Nature,* Vol. 119, 1927, page 674.
[60]*Zhurnal Tehnicheskoi Fiziki,* Vol. 3, 1933, page 1185.
[61]L. Tronstad and T. Höverstad. *Transactions,* Faraday Society, Vol. 30, 1934, page 362.
[62]A. Steinheil. *Annalen der Physik,* Vol. 19, 1934, page 465.
[63]Wm. Shutt and A. Walton. *Transactions,* Faraday Society, Vol. 30, 1934, page 914.
[64]J. Steiner and L. Kahlenberg. *Transactions,* American Electrochemical Society, Vol. 66, 1934, page 205.
[65]W. J. Müller, H. K. Cameron anl W. Machu. *Monatsheft,* Vol. 59, 1932, page 73.
[66]G. D. Preston. *Philosophical Magazine,* Vol. 17, 1934, page 466.
[67]G. I. Finch and A. Quarrell. *Proceedings,* Physical Society, Vol. 46, 1934, page 148.
[68]F. N. Speller. *Mechanical Engineering,* Vol. 51, 1929, page 431.
[69]E. Müller. *Zeitschrift für Elektrochemie,* Vol. 36, 1930, page 963.
[70]Wm. Shutt and A. Walton. *Transactions,* Faraday Society, Vol. 29, 1933, page 1209.
[71]L. Tronstad and T. Höverstad. *Zeitschrift für Physikalische Chemie,* Vol. 170, 1934, page 172.
[72]L. Tronstad and C. Borgmann. *Transactions,* Faraday Society, Vol 30, 1934, page 349.
[73]G. P. Thomson. *Proceedings,* Royal Society, Vol. 128A, 1930, page 649.
[74]A. W. Hothersall. *Journal,* Electroplaters' and Depositors' Technical Society, Vol. 7, 1932, page 115.
[75]L. Tronstad. *Det kongelige Norske Videnskabers Selskabs Skrifter,* Vol. 1, 1931, page 99.

Martensite and Austenite in Hardened Steels

Their Transformation Temperatures

By BENGT KJERRMAN

Metallurgist, SKF, Göteborg, Sweden.

THE TEMPERING OF QUENCHED high-carbon steels, on heating to increasingly higher temperatures, is now considered to take place in three stages, and in three rather distinct temperature ranges:

I.—*At about 100 deg. C.* Martensite which on quenching had a tetragonal body-centered crystal lattice changes to martensite having a body-centered cubic lattice. At the same time appreciable precipitation of the carbon dissolved in the martensite occurs. On continuous heating above this temperature, up to, say, 230 deg. C., virtually all of the carbon held in solution in the martensite precipitates out. The retained austenite, however, remains undecomposed.

II.—*At about 240 deg. C.* The retained austenite breaks down to martensite, which is in turn tempered and most of the carbon precipitated.

III.—*At about 300 deg. C.* Marked coalescence of cementite begins, although for ordinary tempering intervals the cementite cannot be recognized as discrete microscopic particles until somewhat higher temperatures are reached.

The tempering stages outlined above are well illustrated in Fig. 1 showing the changes in electrical resistance in a 1.22 per cent carbon steel on tempering through these temperature ranges. A rapid drop in the electrical resistance begins at just below 100 deg. C. denoting the change from tetragonal to cubic martensite, and a similar sharp drop at about 250 deg. C. denoting the break down of retained austenite.

Now these changes occurred after heating intervals of ½ hr. at the temperatures indicated. The question arises whether the temperature ranges would be lower if the heating intervals were greatly lengthened. Thus, would tetragonal martensite change to cubic martensite at temperatures considerably below 100 deg. C. if the specimens were held at such temperatures for a very long time? Similarly, would austenite break down to martensite at much lower temperatures than 240 deg. C. if the tempering were only prolonged sufficiently?

A positive answer to these questions seemed to have been obtained by Müller[1] who made hardness measurements of a 1.32 C, 0.35 Mn, 0.20 Si, and 0.66 per cent Cr steel after tempering for lengthy periods at 100 deg. C. After 500 hrs. tempering there was a gradual rise in hardness, the rise continuing up to 3000 hrs. (125 days) tempering. Müller concluded this signified that austenite may be decomposed on tempering at 100 deg. C. for lengthy periods. However, in the absence of other confirmatory evidence of the diminution in the amount of austenite on tempering at 100 deg. C. (for example, from X-ray or magnetic data) this conclusion could still be questioned.

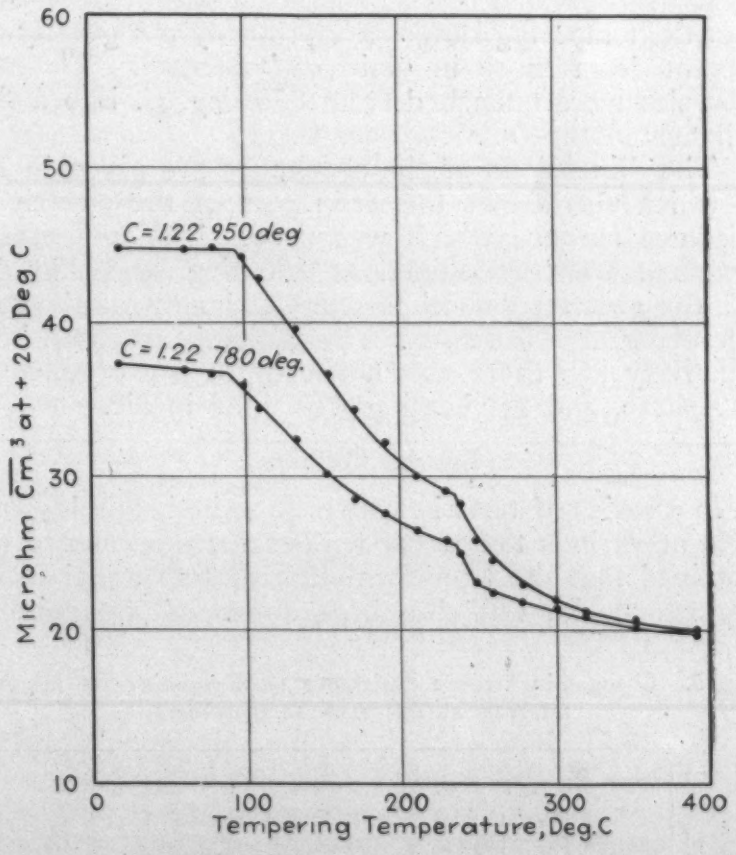


Fig. 1. Changes in Electric Resistance after Tempering ½ Hour at the Temperatures Indicated, Enlund[2]. One sample was quenched from 950 deg. C. and the other from 780 deg. C. before tempering.

This study was undertaken, therefore, to determine, if possible, the lowest tempering temperature at which martensite begins to transform from a tetragonal to a cubic lattice and the lowest tempering temperature at which austenite breaks down to martensite.

Experimental Procedure

The method employed was, in general, the same as that used by Enlund[2], namely, to measure the changes

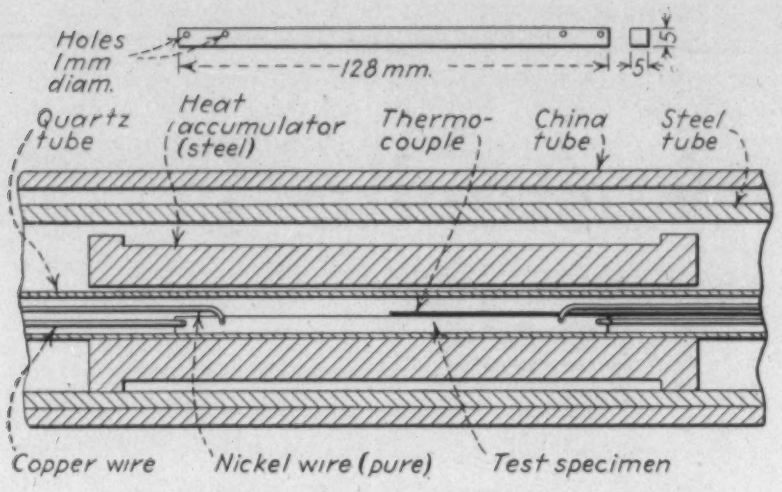


Fig. 2. Electric Resistance Apparatus and Dimensions of the Specimens Used.

in electric resistance of quenched steel specimens upon tempering. Very much longer tempering intervals were used, however, and the electric resistance was measured at the tempering temperature itself, instead of at room temperature after cooling from the tempering temperature.

The steel chosen for study was of the following composition:

	Per Cent
Carbon	1.00
Manganese	1.00
Silicon	0.50
Chromium	1.00

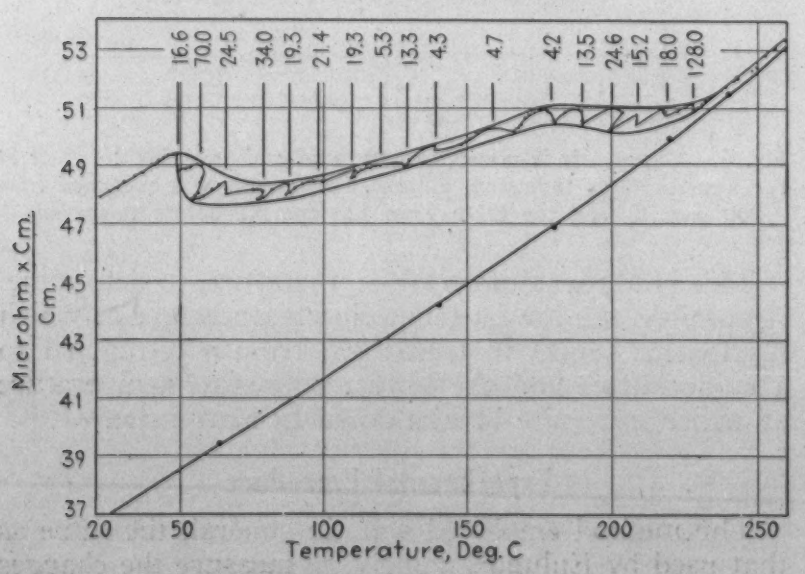
It will be noted that this is not a plain carbon steel, but the tempering ranges are probably not greatly different from those in plain carbon steel. The steel samples were quenched from 830 deg. C. into a light oil heated to 40 to 50 deg. C.

The dimensions of the specimens are given in Fig. 2 which also shows the main part of the electric resistance furnace which was used. The temperature gradient was determined at 186 deg. and 258 deg. C., the greatest deviation over the length of the sample being ± 0.5 deg. C. The temperature used being relatively low there was no need for a protective atmosphere, and the heating was done in air.

Results Obtained

In a series of tests in which quenched samples were held at various tempering temperatures, evidence was obtained that the transformation of tetragonal to cubic martensite and the breakdown of austenite to

Fig. 3. Changes in Electric Resistance on Tempering for Prolonged Intervals at Different Temperatures.



martensite tend to begin and proceed at appreciably lower temperatures than the usually accepted ranges, when the tempering intervals are lengthened. A typical set of curves obtained in one of the tests is shown in Fig. 3. The numbers at the top of the graph give the intervals in hours during which the specimen was held at the temperature indicated. For example, at the first point at which the temperature was held constant, 49 deg. C., the interval was 16.6 hrs.

Even at this low temperature an appreciable drop in electric resistance took place, denoting a change from tetragonal to cubic martensite and the precipitation of carbon. Somewhat similar falls in resistance took place during the intervals at the higher tempering temperatures. Because of these falls in resistance the completed curve, instead of being a line has become a band composed of zigzag lines. The band consists of two separate portions, one approximately between 49 deg. and 80 deg. C., corresponding to the transformation of martensite, and one approximately between 180 deg. and up to 240 deg. C., corresponding to the transformation of austenite. This reaction appeared to be practically completed at 240 deg. C. The smooth line from the upper tempering temperature to a little above 20 deg. C. represents the change

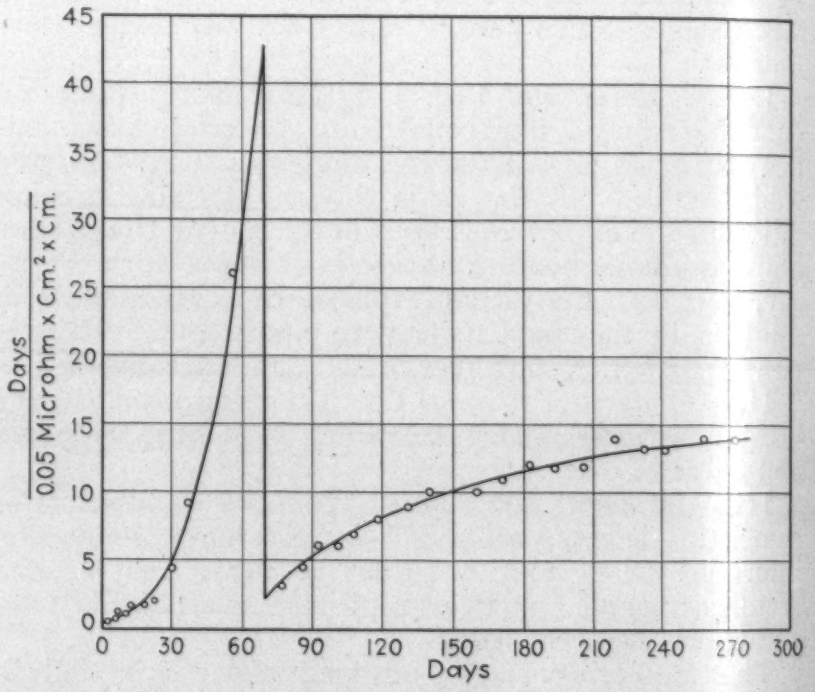


Fig. 4. Rate of Change in Electric Resistance on Tempering at 120 deg. C. for 280 Days.

in resistance as the sample was cooled to room temperature.

Even more striking indications of the extent to which the usually obtained tempering ranges can be lowered by prolonged holding at lower temperatures is given by Fig. 4, which shows the rate of change in electric resistance on holding at constant temperature for a long time. In this case the quenched specimen was first tempered at 153 deg. C. for an hour. After this it was cooled, placed in the apparatus, the temperature raised to 120 deg. C., and then held constant for 280 days.

It will be seen that the curve of Fig. 4 consists of two branches, one between 0 and 69 days and the other between 69 and 280 days. The first branch appears to correspond to the transformation of the martensite which remained after the preliminary tempering for 1 hr. at 153 deg. C. The second branch may denote the beginning of the transformation of austenite, although there is some question about this.

Discussion

The tests indicated that the transformation of martensite as well as the breakdown of austenite depends largely upon the length of tempering time. If the tests are made at the tempering intervals generally used, the martensite begins to transform at about 100 deg. C. and retained austenite begins to break down at about 240 deg. C. But for prolonged intervals these temperature ranges may be appreciably lowered. Indications of the beginning of the transformation of martensite were obtained on tempering at as low a temperature as 40 deg. C., but for still longer tempering times this might have been lowered even further. It appeared probable that untempered martensite is in a labile state at room temperature and that a certain amount of martensite transformation may occur on aging at room temperature. Retained austenite is not decomposed at room temperature. On the contrary it does not appear that austenite begins to decompose even at above room temperature until the martensite has been transformed from tetragonal to cubic.

The above conclusion is based mainly on the evidence shown in Fig. 4. It should be recalled that the temperature was kept constant during the whole test so that the two types of behavior denoted by the two branches of the curve must represent two reactions, the second of which did not begin until the first was completed.

Possibly the second branch of the curve represents the beginning of the decomposition of retained austenite after prolonged heating at 120 deg. C. However, it may perhaps indicate an increased rate of carbon precipitation from martensite. Attempts were made on similar samples treated in the same way to determine by X-ray diffraction studies whether there had been a decrease in the amount of retained austenite. No appreciable decrease was indicated, but possibly a small part of the retained austenite (too small to be detected by the X-ray method) did decompose. At any rate, it was clear that long heating at 120 deg. C. did not decompose any large proportion of the retained austenite.

Some of the above discussion has been given by the author in a Swedish publication[3] in more extended form.

Bibliography

[1] Müller, H. "Ein Beitrag zum Problem der Stahlhärtung." *Forschungsarbeiten über Metallkunde u. Röntgenmetallographie*, No. 7, 1932, 66 p.

[2] Enlund, B. D. "On the Structure of Quenched Carbon Steels." *Journal*, Iron and Steel Inst., Vol. III, 1925, pp. 305-314.

[3] Kjerrman, B. "Martensitens och restanstonitens omvandlungstemperaturer." *Jernkontorets Annaler*, 1935, No. 6, pp. 217-231.

EDITORIAL COMMENT

(Continued from page A25)

a propaganda article even when it really doesn't fall in that class.

It is odd that such groups are not more often shrewd enough to get the very same thing written up by the satisfied user instead of doing it themselves. When a user is willing to go on record, neither the editor nor the reader bristles up with conscious or subconscious disbelief.

Handouts telling in vague terms of a wonderful laboratory development, without details, are another irritation. They may have news value, for a real description may be forthcoming as soon as the patent nuisances are cleared up, but the more knowing firms wait till they can make their first blow a telling one.

It would be much simpler to print all such stuff as it comes in, as far as space will permit, than to get it rewritten when it has value but is poorly served up in some details, or to refuse it and search for material of real value. But it seems to us not only unwise to trust that propaganda will always carry its own antidote in the case of real propaganda, but also unfair to the technical departments of firms whose technical data have to pass through a re-writing by the advertising department which gives it just the wrong flavor to be palatable to engineering readers and makes it fall unnecessarily into the propaganda classification in their minds, when the propaganda is only apparent, not real.

Anyhow, we hope that through November at least, we may be spared from having to cope with real or apparent propaganda, for we will have much and plenty from the politicians without any from the technicians.—H. W. G.

"Shirt Sleeve" Metallurgists

IN the annual report of one of the large American steel companies, the following comment, with some deletions, is of interest:

> A large share of credit for operating and sales successes can be laid at the door of the metallurgical department. In the merchandising of steel products, the responsibility of the mill does not cease when the shipment is made. The products must do the jobs they are made to do—they must fabricate successfully and economically. To the large staff of metallurgists, the proper use and fabrication of products are direct responsibilities.
>
> While many of these men have brilliant records in theoretical research, "applied shirt-sleeve metallurgy" has been responsible for (the company's) reputation for outstanding engineering service to customers. For every metallurgical trouble-shooter in the field, there are three metallurgists backing him up in the laboratories. When a trouble call comes in from the field, a field man is put on the job and put there quickly. Practical men are these metallurgists, well fitted by education and experience to iron out all sorts of production problems and to tackle any sort of job at any time.

"Applied shirt-sleeve metallurgy" is an excellent designation for a phase of activity which is not only as important as indicated, but which is wide spread. The "applied shirt-sleeve metallurgist" is a vital factor in the success of a steel company's operations. Most of the large and some of the smaller steel producers have such a staff of men. They supplement the regular metallurgists confined to the plants, many of them specializing in a definite line of products.

With the advent of the long list of low-alloy, high yield strength steels with their applications, and the greater use of alloy and special steels in general, the need for this type of men will expand. And to meet this demand special knowledge and experience are requisite. Which goes to emphasize how vital to the all-around successful steel company are, not only this brand of metallurgist, but also the plant and the research investigator.—E.F.C.

Note on Annealing Twins in Ferrite

By ALLAN L. TARR

Instructor in Metallurgy, Cooper Union Inst. Tech., New York City

DURING THE MICROSCOPICAL examination of some Armco iron some interesting features in structure were observed, and are described and illustrated in this note.

Figs. 1 and 2 show well defined annealing twins. These twins are defined by clear straight lines and appear on cut, ground, polished and etched surfaces, as well as on the vaporization "etch" surfaces. The former are obviously ferrite. They do not resemble Neumann band mechanical twins in any of their characteristics.

The treatment which is responsible for their formation is as follows:

> Heat treated in moist hydrogen at 1490 ± 10 deg. C. for 18 hrs., cooled to 890 deg. C. in 1 hr., then annealed at 890 deg. C. for 12 hrs., followed by slow cooling to room temperature.

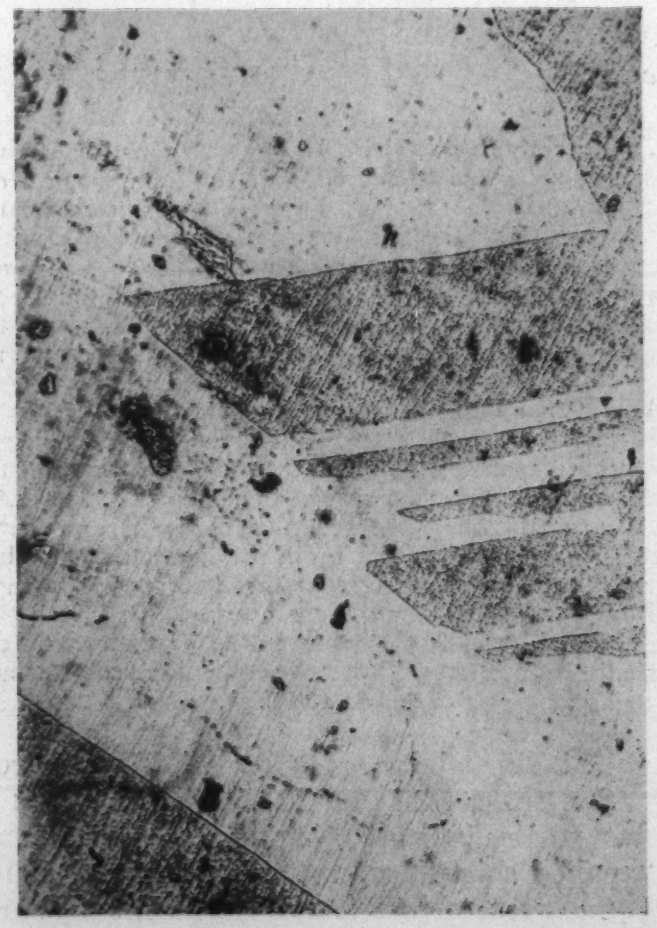


Fig. 1. Annealing Twins of "Pure" Iron. Silicon 0.01 per cent min. Carbon, probably only trace. Polished, and etched with 5 per cent Nital. Magnification, 100 diameters.

The samples were in the form of plates 3/32 by 2 by 5 in. several layers, each partially separated by a single turn of fine iron wire. The treatment reduces carbon, sulphur, phosphorus, oxygen and nitrogen to very small quantities. Silicon, manganese, copper and aluminum are not reduced. (P. P. Cioffi, *Physical Review,* pp. 363-367, Vol. 39, No. 2, Jan 15, 1932.)

It should be noted that the vaporization etch appears only on the inner surfaces of the pile of plates —the surfaces directly exposed to hydrogen do not show the twin structure by vapor etch. However, there is a coarse grain boundary which appears on all surfaces—these polyhedral grains are usually six or eight sided. Such grain outlines have obviously been produced by slippage of crystals—probably delta crystals. These grains are depressed on one side of a plate and protrude on the opposite side.

It should be noted further that the vapor etch twin structure is completely eradicated by an acid etch and larger grains are revealed. The latter are occasionally twinned. On some vapor etch surfaces there are three grain boundary outlines (delta, twinned bands and thin polyhedral outlines) and, if these are acid etched, a fourth grain outline replaces all of the others.

I have not seen any pictures of ferrite annealing twins and these notations are made simply to show that they may be developed in purified iron.

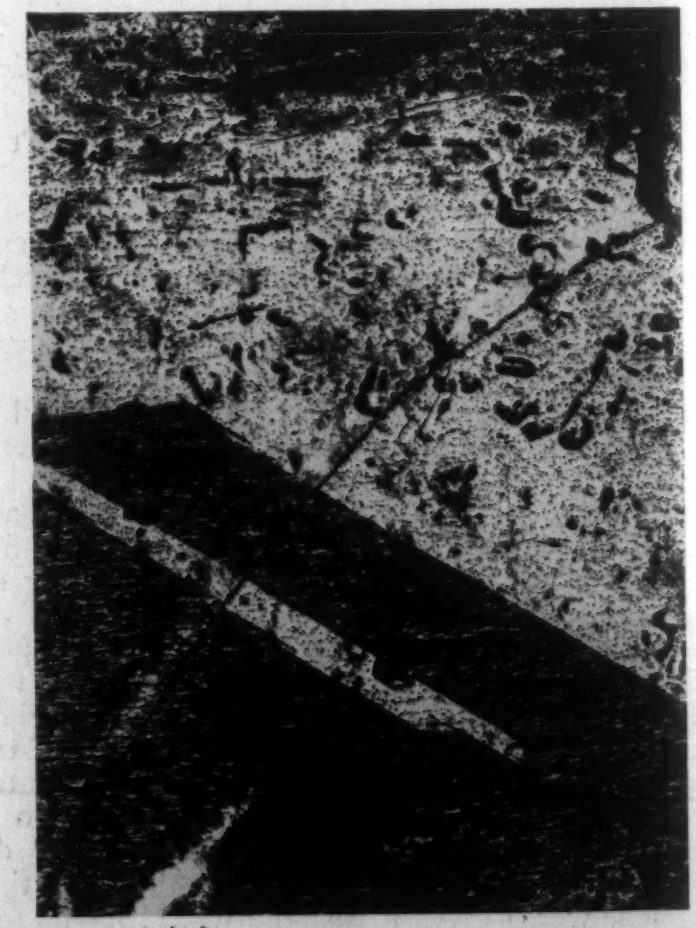


Fig. 2. Annealing Twins of "Pure" Iron. Composition same as Fig. 1. Vaporization "etch." Note: Secondary grain boundary. Magnification, 30 diameters.

At present it is not convenient to make a complete analysis of the significance of the several grain boundaries. Cioffi states, "There is evidence that the large grains grow at the high temperature and that under certain conditions retain their identity even after cooling through two transformation points." If this is correct, it is not easy to account for three other grain boundary lines.

Small Plastic Deformations in Strip Steel

Directional Properties, Caused by These, Detected by X-Ray Diffraction

By NORMAN P. GOSS

Chief Physicist, Cold Metal Process Co., Youngstown, Ohio

SEVERAL INVESTIGATORS[1] REPORT in the literature that X-ray diffraction methods are not sensitive enough to detect directional properties introduced into strip steels and other metals by subjecting them to slight plastic deformations in the range of 0 to 15 per cent. The purpose of this paper is to show that the X-ray diffraction methods can determine the presence or absence of directional properties imparted to steel or other metals when given such small degrees of plastic deformation.

It is not very difficult to detect even the slightest amount of preferred orientation present in the strip steel specimen, provided the X-ray beam is transmitted in the proper direction. The proper direction may be defined as the one in which preferred orientation appears with the smallest amount of cold working. When the X-ray beam is transmitted perpendicularly to the surface of a cold rolled strip, one finds that a very large amount of cold rolling is required before preferred orientation of the grain units appears. However, when the X-ray beam is transmitted in a direction parallel to the surface and perpendicularly to the direction of rolling, preferred orientation of the grain fragments can in some instances be detected when the area reduction is only 5 per cent. The smaller the grain size, the less the amount of cold working required to introduce directional characteristics.

In most commercial hot rolled strip, which has been heat treated so as to remove all traces of preferred orientation, and in which the grain size will vary from 0.001 in. to 0.004 in. diameter, preferred orientation of the grains is developed with an area reduction of 10 per cent or less when X-rayed in the proper direction. It should also be noted that only an area reduction of 5 per cent fragments the grains considerably, and the X-ray diffraction patterns, as will be seen later, show this very clearly.

In round wires[2] the crystal fragments are oriented when given an area reduction of only 5 per cent, provided the grain size is under 0.002 in. in diameter. The X-ray beam in this case is transmitted at right angles to the wire axis, since the grain fragments are always oriented at random about the wire axis, but definitely oriented along the wire axis.

The orientation of the crystal fragments in cold rolled strips is somewhat more complex, but quite easy to determine. In many specimens, which had been given an area reduction of over 60 per cent, no definite amount of preferred orientation of the grain fragments could be detected when the X-ray beam was transmitted normally to the surface of the strip. However, where the X-ray beam was transmitted in a direction parallel to the surface and at right angles to the rolling direction, a very intense fiber pattern was obtained. This direction, I prefer to call the "principal direction", since it is the one in which the preferred orientation of the grains appears to develop most rapidly and intensely.

Several years ago the writer made an exhaustive study on strip steel specimens having various grain sizes in the annealed condition ranging from 0.0005 to 0.010 in. in diameter. These strips were given area reductions varying from 2 to 80 per cent. These experiments proved beyond doubt that the smaller the grain size, the smaller the amount of cold rolling required to introduce preferred orientation when X-rayed in the principal direction.

These experiments also revealed a very interesting fact, in that the directional properties appear to develop more rapidly after grain fragmentation is complete.[3] In this paper the X-ray diffraction diagrams prove that the larger the grain size, the greater the amount of cold working required to completely fragment the grains into smaller units.

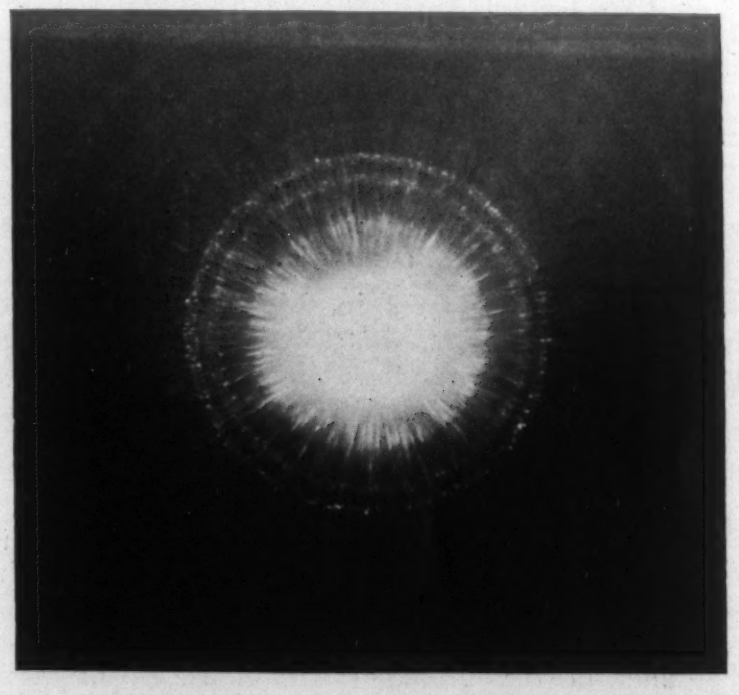


Fig. 1. X-Ray Diffraction Pattern of Low Carbon Strip Steel (0.100 in.) Heat Treated at 1650 Deg. F., 2 hrs.

In the case of commercial strip steels, the grains are usually completely fragmented with an area reduction of only 25 per cent. We must interpret this in the following way:

In the original material, which is in the heat treated condition, the diffraction rings are made up of a large number of discrete spots which are more or less sharply defined. However, after such a specimen has received an area reduction of only 25 per cent, these spots are completely obliterated.

For example, in Fig. 1 the diffraction rings are composed of a large number of discrete spots. Fig. 5 is an X-ray diffraction pattern made of the same

strip steel after it had been given an area reduction of 25 per cent. The rings are now smooth in appearance. This amount of cold work has completely destroyed the identity of the individual spots so conspicuous in the X-ray diffraction pattern of Fig. 1. With continued cold work, the texture of the rings does not change, except that the degree of preferred orientation only changes. See Fig. 6.

Insofar as the X-ray particle size is concerned, we see that it does not change after fragmentation is complete, but the degree of preferment certainly does. This fact seems to have some support from hardness tests on hot rolled strip given various percentages of cold work by cold rolling. This important point will be discussed more appropriately later on under experimental evidence.

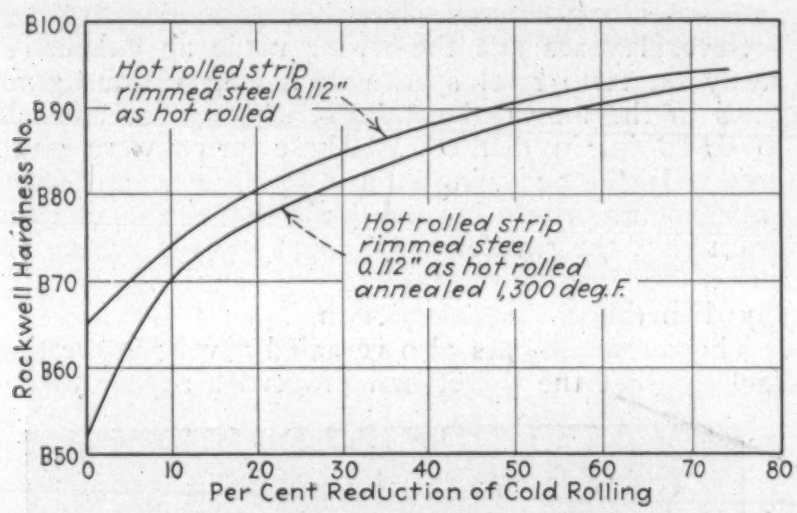


Fig. 1A. Change in Hardness as Related to the Amount of Cold Work the Specimen has Received.

Experimental Evidence and Interpretation of X-Ray Diagrams

A hot rolled strip 0.100 in. thick, having the following chemical analysis, was selected for this investigation;

	Per Cent
Carbon	0.08
Manganese	0.43
Phosphorus	0.012
Sulphur	0.025

A strip 2 in. x 6 in. x 0.100 in. thick was heat treated for two hours at 1650 deg. F. in a slightly reducing atmosphere. Before cold rolling, an X-ray examination was made by taking a number of X-ray diagrams in the principal direction. Examination proved the strip to be free of any residual preferred orientation. Fig. 1 is the X-ray diffraction diagram of this strip, and it meets the requirements. The grains were about 0.002 in. to 0.003 in. in diameter, and are distributed entirely at random.

The grains, however, are not perfect in structure. The small spots in the first two rings (K_a and K_b) are due to reflections from the (110) planes, many of which are not sharply defined. This means that the grains are quite imperfect in crystal structure.

The annealed strip was given an area reduction of 5 per cent by cold rolling. After this operation, another specimen was prepared for X-ray examination in the principal direction. It is apparent from Fig. 2 that this amount of cold work has severely fragmented the grains. The diffraction spots which were quite sharply defined in Fig. 1 are now much more diffuse, and the ones which were ill defined are now even more diffuse in structure. This amount of cold working did not introduce preferred orientation, but did break the equiaxed grains into smaller units.

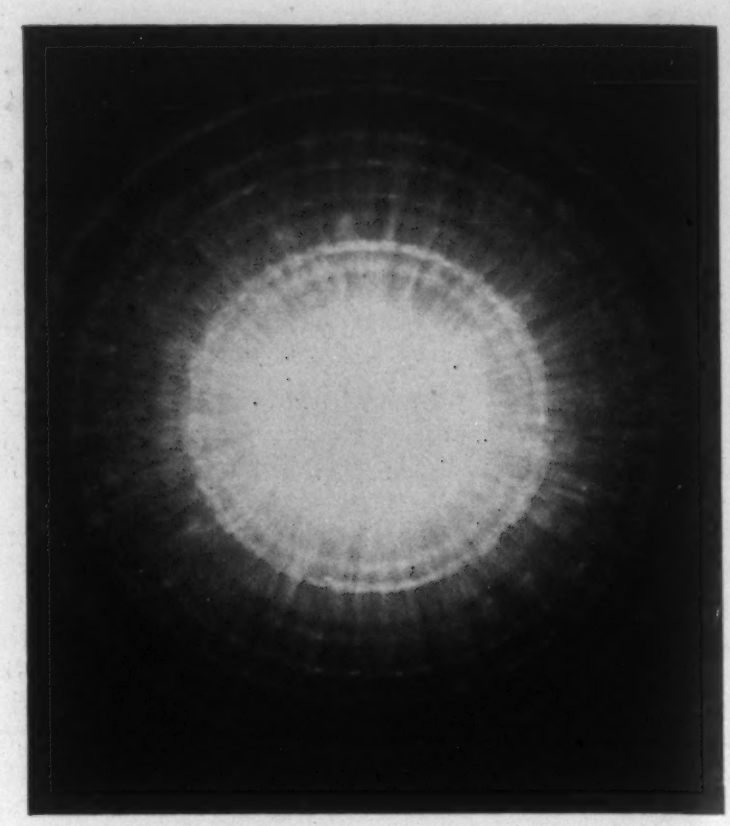
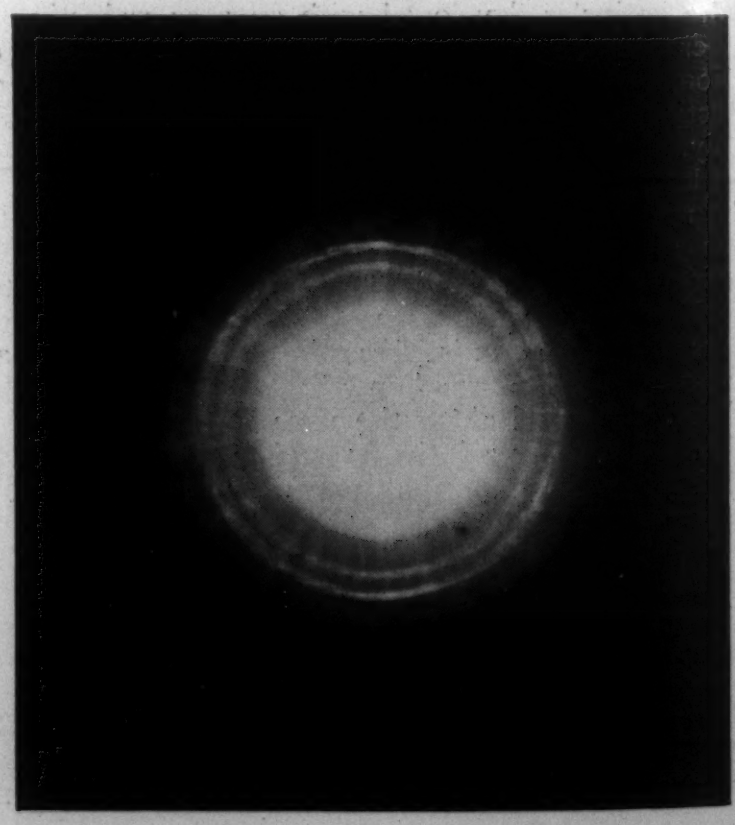


Fig. 2. X-Ray Diffraction Pattern of a Low Carbon Strip Steel, Heat Treated at 1650 Deg. F., 2 hrs. Area reduction, 5 per cent.

The diffuseness of the diffraction spots must not be interpreted to mean that the atomic space lattice has been strained[4], but clearly shows that the equiaxed grains as seen under the microscope have been fragmented into smaller units which are displaced statistically from the original orientation of the parent grain. Furthermore, the parent grains prior to fragmentation by cold working were composed of smaller units. In short, we find that in most commercially heat-treated materials the grains are mosaic in structure. When the X-ray diffraction patterns are interpreted in this way we find that the grains in annealed metals and in slightly worked metals are actually complex structures, about which very little is known, and much remains to be determined and investigated.

This same specimen was then given an area reduction of 10 per cent, and another X-ray diffraction

Fig. 3. X-Ray Diffraction of Low Carbon Strip Steel, Heat Treated at 1650 Deg. F., 2 hrs. Area reduction, 10 per cent.



pattern made in the principal direction. Fig. 3 shows that continued cold working by cold rolling has fragmented the grains into still smaller units, and these are deviating more and more from the orientation of the parent grains of the original heat-treated material.

The individual spots which were quite clearly defined in Fig. 1 are nearly, but not completely, obliterated. The grains have been fragmented into smaller particles and are being gradually oriented into a new definite direction. The preferred orientation of the grain fragments at this stage of cold working is not very sharply defined, but definitely present.

After cold rolling 15 per cent (0.100—0.085 in.) the X-ray diffraction pattern as shown in Fig. 4 is obtained. Grain fragmentation has greatly increased, and the directional properties are more sharply defined.

On the other hand, R. Mehl and M. Gensamer could not find any evidence of preferred orientation in specimens given area reduction as much as 40 per cent. They concluded, to quote: "This is a severe limitation in the X-ray method, though it is possible

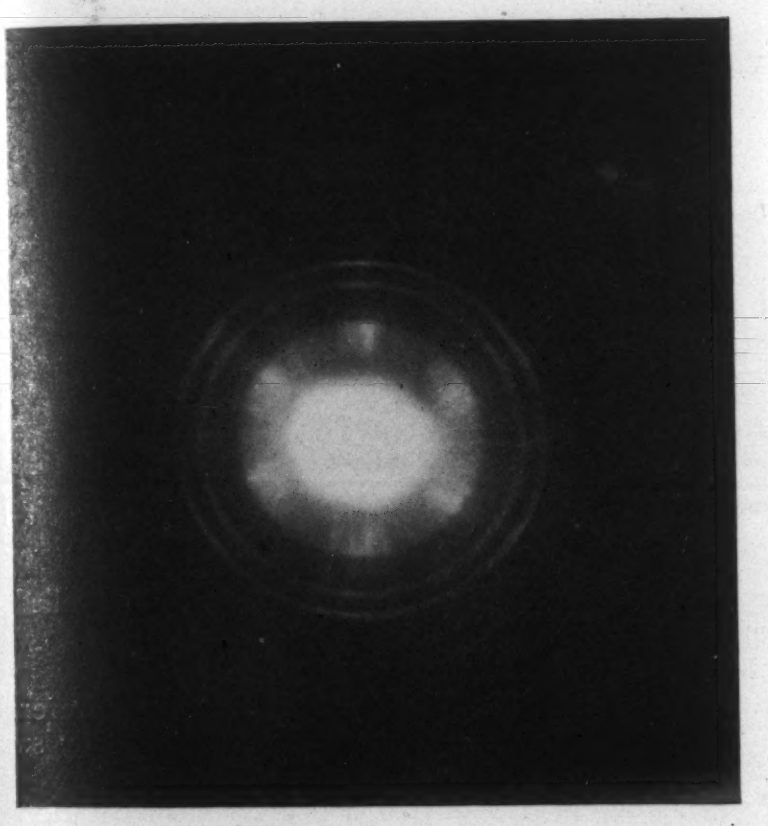


Fig. 4. X-Ray Diffraction Pattern of Low Carbon Strip Steel, Heat Treated at 1650 Deg. F., 2 hr. Area reduction, 15 per cent.

that special technique might be developed to give better results".

These results clearly show that no special X-ray methods are required, the only requirements being to X-ray the specimen in the proper direction. Figs. 5 and 6 were made of the same specimen after it had received 25 and 75 per cent area reduction. The only essential difference is that in Fig. 6 the grain fragments are more sharply oriented. Insofar as the X-ray diffraction evidence is concerned, grain fragmentation is complete when the area reduction is 25 per cent. The diffraction rings of Figs. 5 and 6 appear to be the same insofar as the texture is concerned, but the grain fragments are more sharply oriented in Fig. 6. This observation is supported by hardness tests, as already mentioned previously in the text.

Fig. 1A is a curve showing the change in hardness as related to the amount of cold work the specimen has received. It is clearly seen that the rate of hard-

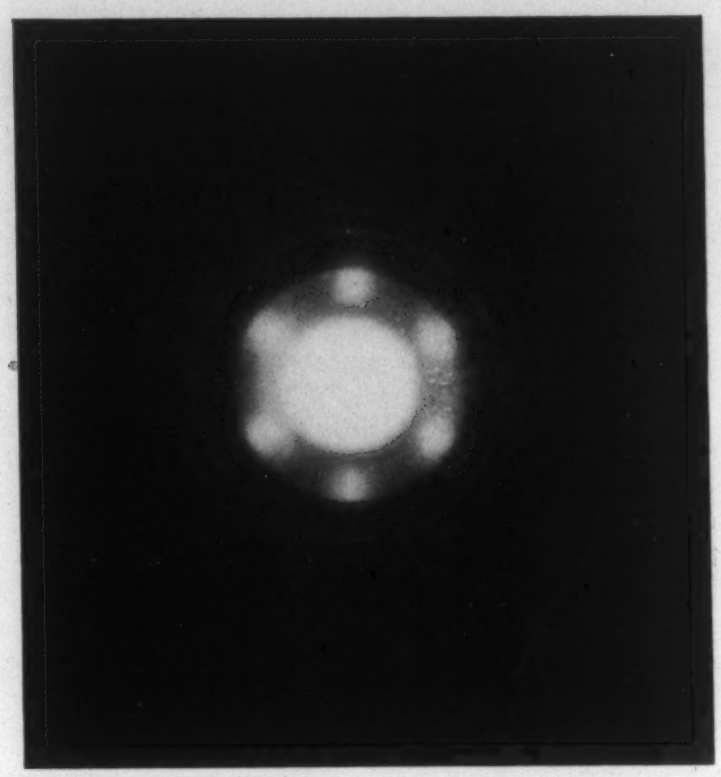
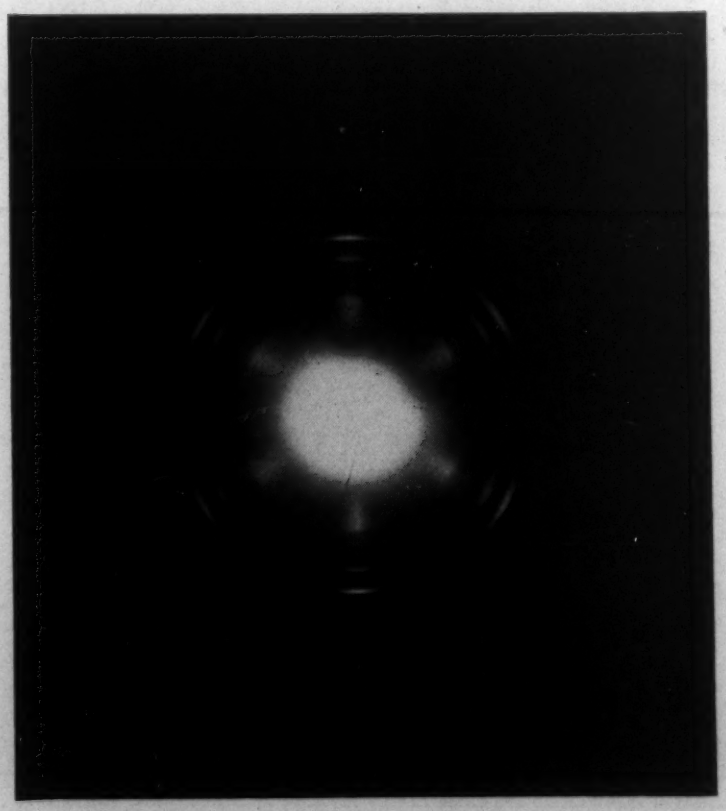


Fig. 5. X-Ray Diffraction Pattern of Low Carbon Strip Steel, Heat Treated at 1650 Deg. F., 2 hrs. Area reduction, 25 per cent.

ening is most marked in the earlier stages of cold working, and much less marked in the final stages. This is certainly in agreement with the X-ray diffraction diagrams presented here, and which show that the grain fragmentation is most marked and drastic in the earlier stages of cold working. In other words, the hardness increases most rapidly for the cold rolling lying between 0 and 25 per cent area reductions, and increases less rapidly between 25 and 50 per cent; and so we see that a correlation between the rate of hardening and the X-ray diffraction pattern exists. This is a very important and interesting point, and deserves more careful consideration. Here, in a preliminary way at least, is shown how the X-ray and hardness tests can successfully be applied to a problem of this type.

In Fig. 7 an X-ray diffraction pattern of a hot rolled strip which had a rather intense fiber structure is shown when X-rayed in the principal direction.

Fig. 6. X-Ray Diffraction Pattern of Low Carbon Strip Steel, Heat Treated at 1650 Deg. F., 2 hrs. Area reduction, 75 per cent.



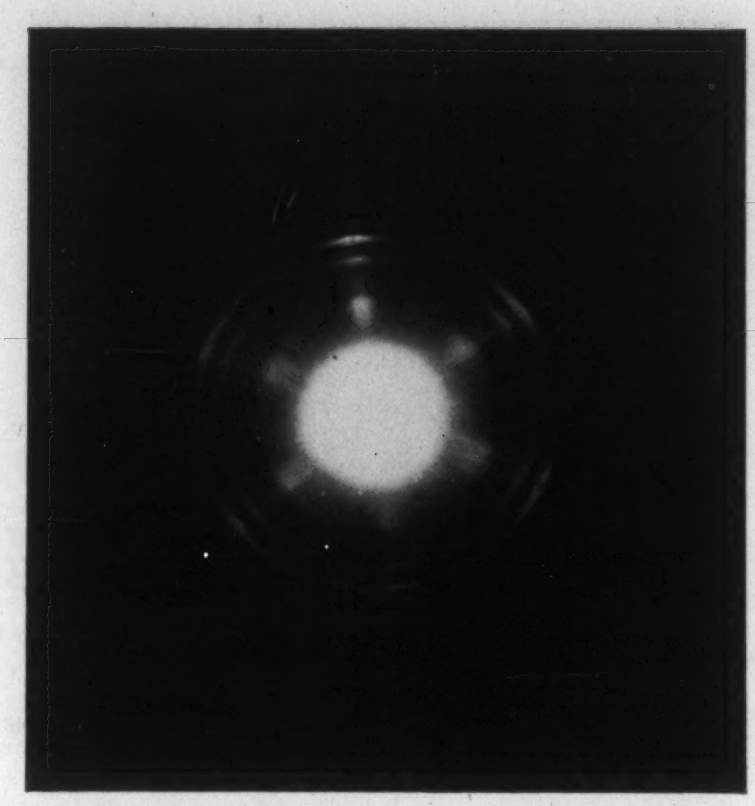


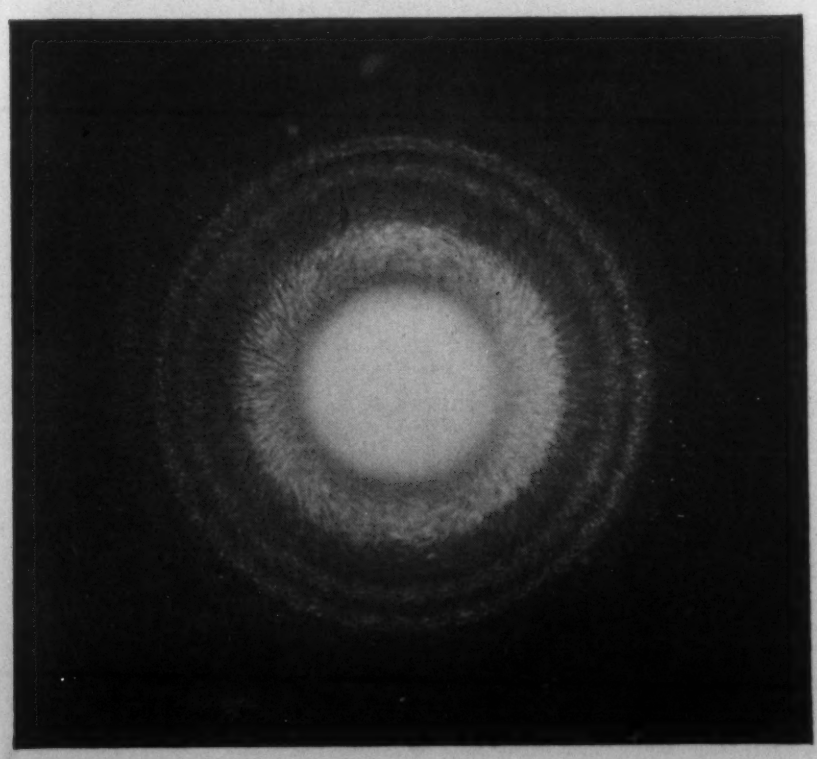
Fig. 7. X-Ray Diffraction Pattern of a Hot Rolled Strip Steel (Low Carbon). X-ray beam transmitted in the principal direction.

When this same specimen was X-rayed by transmitting the X-ray beam normal to the surface, a random grain orientation was found. This again illustrates that it is very important to X-ray the specimen in the proper directions when studying metals for the presence of preferred orientation of the grains. Again, if such a structure as shown in Fig. 7 is cold rolled, say 5 per cent, and X-rayed in the principal direction, an intense fiber structure results; but here most of it is due to hot rolling, and only a very small part can be attributed to the cold working.

In order to detect fiber structure in metals, one must X-ray it properly, and above all, be certain that the specimen is absolutely free of preferred orientation before cold working. This is a very important consideration, and usually entirely neglected.

As a further illustration of this point, one might cite what occurs in the cold drawing of hot rolled rods. When X-rayed at right angles to the rod axis a random grain distribution is always found, as shown in Fig. 8. However, when the beam is transmitted parallel to the axis of the hot rolled rod, a fiber pattern results as shown in Fig. 9.

Fig. 8. X-Ray Diffraction Pattern of a Low Carbon Steel Hot Rolled Rod (No. 5). X-Ray beam perpendicular to rod axis.



When such a hot rolled rod is cold rolled, the fiber pattern develops in the other direction; i.e., a strong fiber structure developed when the specimen was X-rayed at right angles to the wire axis, and a random structure was found when the X-ray beam was transmitted along the wire axis. From this, we see that the fiber structure of the hot rolled rod and the cold drawn wire are at right angles to each other, a very unusual result.

From these considerations, it can be seen that the direction in which the grain units are oriented depends upon the method of working, and differs according to whether the rod or strip was hot rolled or cold rolled.

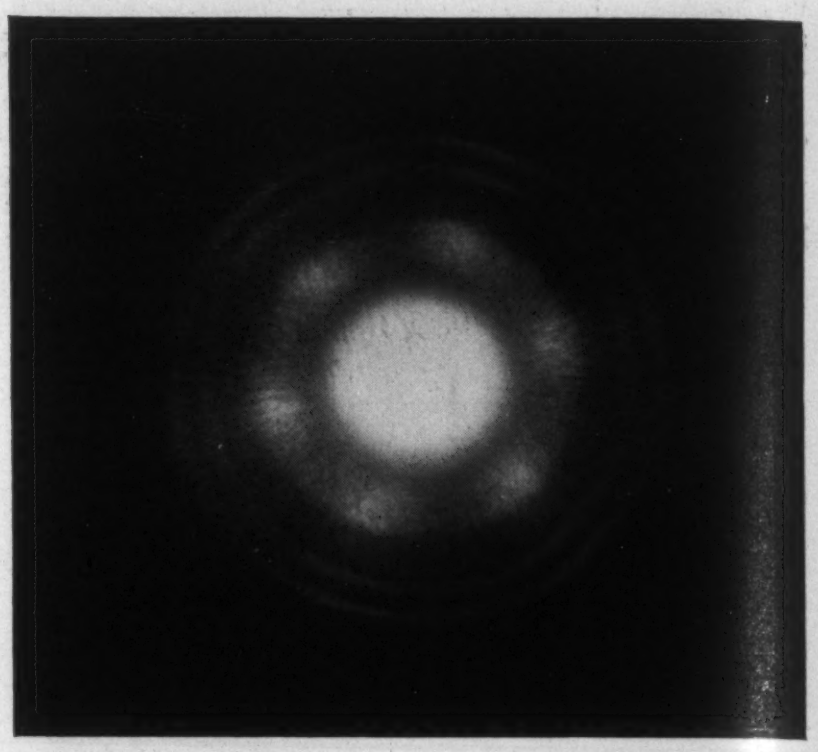


Fig. 9. X-Ray Diffraction Pattern of a Low Carbon Steel Hot Rolled Rod (No. 5). X-Ray beam parallel to axis of rod.

Conclusions

1. X-ray diffraction methods can detect preferred orientation of grain fragments developed by small plastic deformations.
2. Hot rolling also develops preferred orientation in hot rolled strip steels. When such structures are cold rolled, allowance must be made for the directional properties induced by hot rolling.
3. When heat-treated metals are given small degrees of cold work, the grains are fragmented into smaller crystal units. The lattice parameters are not changed by such a small degree of cold work. The diffuseness of the diffraction spots after cold working has been interpreted to mean that the space lattice has been strained, but in this investigation the results show that it is due to grain fragmentation.
4. In hot rolled rods and cold drawn wires, preferred orientation is developed in different directions.

References

[1] A. Phillips and H. H. Dunkle. Directional Properties in Rolled Low Carbon Steel. *Transactions*, American Society for Metals, June, 1935. Discussion by R. F. Mehl and M. Gensamer, page 405. Answer by the authors, page 408.

[2] N. P. Goss. Application of X-Rays to the Study of Plastic Deformation in Steel Wires and Molybdenum Ribbon. *Transactions*, American Society for Steel Treating, Feb. 1930.

[3] N. P. Goss. Fibrous Texture and Mosaic Structure in Single Grains and Polycrystalline Aggregates. (In Press.)

[4] R. F. Mehl and M. Gensamer. An X-Ray Study of Lüders' Lines and Strain Figures in Low Carbon Steel. *Metals & Alloys*, June 1935, page 158.

Magnesium Silicide in 85-15 Brass

Effect on the Properties

BY H. S. VAN KLOOSTER AND J. E. HARRIS, JR.

Rensselaer Polytechnic Institute, Troy, N. Y.

SOME YEARS AGO Gould and Ray[1] studied the effects of silicon (up to 10 per cent) on the properties of 85-15 and 60-40 brass. Since both silicon and magnesium silicide (Mg_2Si) are hard and brittle materials, it might be expected that the latter has somewhat similar effects on brass. From the investigations of Hanson and Gayler[2] and those of Honda[3], it appears that magnesium silicide aids in the aging of aluminum alloys of the duralumin type. The work here presented was undertaken in the hope that addition of this compound would produce beneficial results with certain types of brasses.

Some preliminary work had been carried out in 1931 by L. J. Allard[4] who added up to 6 per cent Mg_2Si to cartridge brass (2 to 1) and found that, with decreasing density (from 8.49 to 7.14), a corresponding increase in hardness was noticed in chill cast samples. Annealing at 130 deg. C. increased the hardness somewhat while heating at 550 deg. C. decreased the hardness in all cases. The age-hardening effect was hardly perceptible. In 1934, W. D. Warren[5] added from 1.0 to 3.2 per cent magnesium silicide to a 74-26 brass and found, likewise, that the hardness of chill cast specimens increased linearly with the percentage of added compound. (From E. 46 Rockwell, to about 104 for the 3.2 per cent magnesium silicide alloy.) The brasses containing the compound were stiffer and considerably less ductile on the lathe than the plain brass, the drillings falling off in chips instead of forming helical turnings. Here again, no appreciable age-hardening effect was detected.

Preparation and Analysis of Magnesium Silicide

Magnesium silicide contains 36.8 per cent silicon and is prepared by direct fusion of magnesium and silicon. Vogel[6] first prepared the pure compound in small test tubes of graphite in an atmosphere of hydrogen and obtained it as a hard, brittle, bluish-grey, metallic product which melted at 1102 deg. C. Some years later it was synthesized by Wöhler and Schliephake[7] who confirmed the work of Vogel. Warren[5] succeeded in making the compound in batches of 100 grams or more by first melting the magnesium under a flux of magnesium-potassium chloride in Battersea crucibles (type D) which were covered with perforated carbon plates through which the silicon was introduced in small lumps. The magnesium was used in about 10 per cent excess of the required amount and when molten, the temperature was gradually raised during the addition of the silicon. The molten alloy was poured in an inclined iron mold. The uncombined magnesium invariably burned off during the pouring with a vivid white light. The flux remaining on the surface of the solidified product was removed by washing. The specific gravity (at 20 deg. C.) was found to be 1.95, which agrees with the value given by Owens and Preston[8].

In the final experiments, reported below, the magnesium silicide used was furnished by the Magnesium Co. of America in the form of a granular material (specific gravity 1.94). The analysis proved to be rather difficult and time-consuming. After thorough grinding and several evaporations to dryness with dilute nitric acid, the silicon dioxide residue was filtered off and saved. The filtrate was again boiled down and the silicon dioxide obtained from the filtrate was added to the first residue. The magnesium was determined from the filtrate in the usual manner. The values obtained for magnesium agreed closely with the theoretical value (63.2 per cent) but the results for silicon were all too low. The fact is undoubtedly due to the loss of silicon during the solution process, rather than to any impurity of the compound.

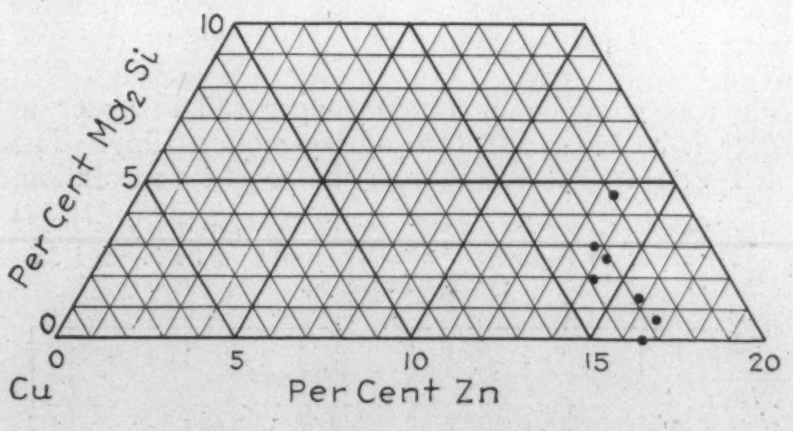


Fig. 1. Composition of the Alloys.

Preparation and Analysis of the Alloy Brasses

The electrolytic copper used in preparing the brasses was in the form of a large cube, 4 in. on a side,

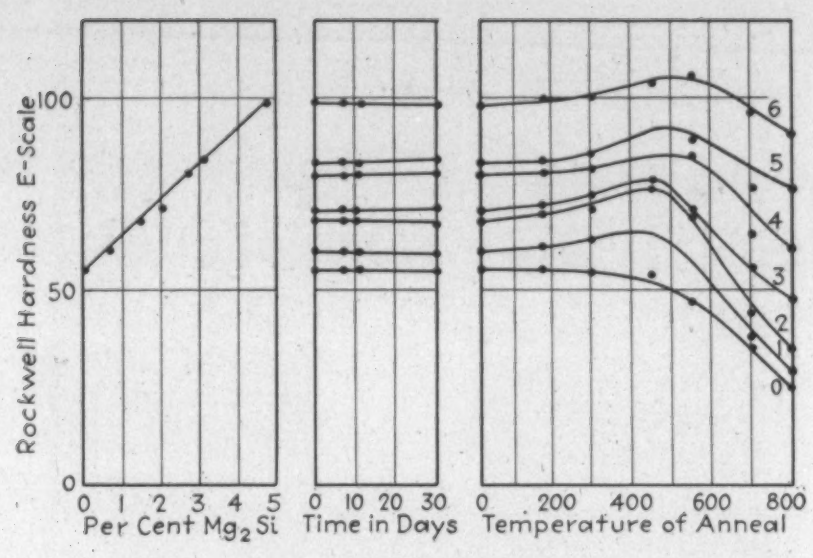
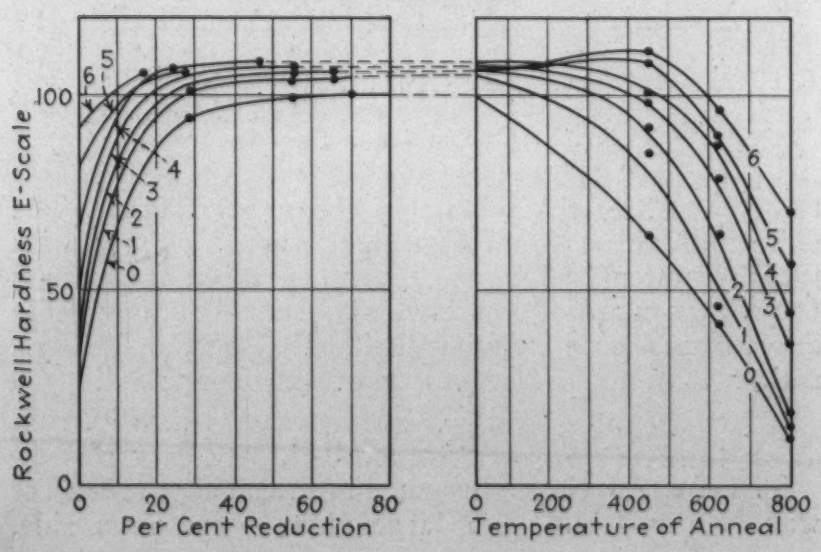


Fig. 2. Hardness of the Chill-Cast Samples of the Alloys Varies Almost Linearly with the Percentage of Magnesium-Silicide.

taken from a wire bar. Pieces of convenient size were obtained by drilling the cube with an automatic drill. The zinc was in the form of a large flat cake which was broken into suitable sizes by chiseling and sawing. In order to get a considerable amount of zinc to dissolve at a temperature well below its boiling point, a 50-50 brass was first made in a gas-fired furnace. The mixture was fused in large Battersea crucibles and melted around 880 deg. C. By comparing the amount of brass with that of the materials, it was found that a considerable amount of zinc was lost. An excess of about 10 per cent zinc was required in order to bring the copper with the 50-50 brass added, up to the required 85-15 percentage. Altogether about 3000 grams of brass were prepared.

This charge was placed in a graphite crucible, covered with powdered charcoal to prevent oxidation, and heated in an Ajax-Northrup high frequency furnace, operated on 8000 watts. Melting occurred in about 25 min., after which period part of the melt was poured into a three-fingered iron mold, which had been preheated to secure complete filling of the first two fingers. The mold was opened at once after pouring so the hot alloy could be chilled to room temperature under the tap within one minute after pouring. The alloys containing magnesium silicide were made up by adding the compound to the rest of the same melt. The granular magnesium silicide was wrapped in a thin copper foil in order to force it below the surface of the molten alloy. The melt was stirred to secure a homogeneous solution.

Fig. 3. Effect on Hardness of the Alloys of Cold Rolling and Subsequent Annealing.



When most of the compound had dissolved (some of it having been ejected from the crucible) enough of the melt was poured in the iron mold as before, whereupon magnesium silicide was again added to the melt in a quantity sufficient to give a 2 per cent alloy. The dissolving and pouring was continued and four other alloys, theoretically 3, 4, 5, and 8 per cent of magnesium silicide, prepared. The total procedure required about 2 hrs. so that comparatively little zinc was lost.

All alloys were subsequently analyzed. The copper content was determined in all samples in triplicate, in the usual way, by electrolysis. Magnesium was determined in duplicate in all six alloy brasses. The silicon content was calculated from the magnesium, since there was no loss of silicon in the compound and zinc was computed by difference except in the pure brass and in the last alloy. In these two cases the percentage from analysis agreed with that found by difference. The complete analysis and the composition of the seven alloys is recorded in Fig. 1 and Table I.

Table I—Analyses of the Alloys.

Alloy No.	Cu Per cent	Zn Per cent	Zn Per cent, by difference	Mg_2Si, Per cent (from $Mg_2P_2O_7$)
0	83.43	16.30	16.57	0.00
1	82.76	....	16.58	0.66
2	82.78	...	15.77	1.45
3	83.71	....	14.24	2.05
4	83.09	....	14.24	2.67
5	83.24	....	13.72	3.04
6	81.85	13.63	13.43	4.72

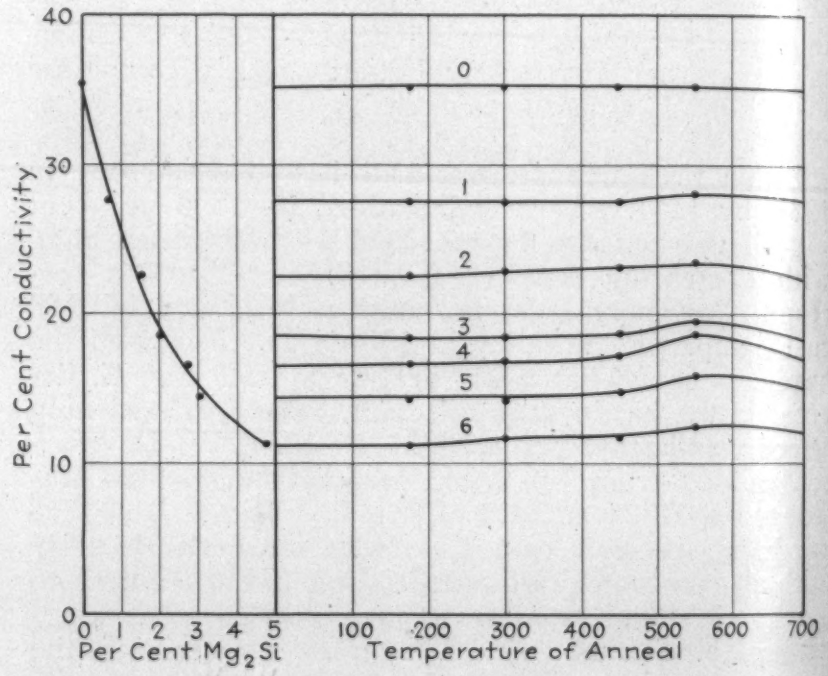


Fig. 4. Effect on Conductivity of the Alloys as Cast and after Annealing.

Physical and Mechanical Properties

The following properties were investigated: Density, hardness, conductivity, thermal behavior, microstructure. The density (d_4^{20}) for the seven specimens in the order indicated above decreased from 8.75 for the pure brass through 8.63, 8.46, 8.42, 8.32, 8.29 to 8.05 for the specimen containing 4.72 per cent magnesium silicide.

The hardness was measured on a Rockwell machine, on a deep-V anvil with a 1/8-in. ball penetrator by employing a 10 kg. minor load and 100 kg. major load. The readings thus obtained are on the Rockwell E scale. Measurements were made at distances about 5 mm. apart, along the length of the sample. They varied somewhat, so that in each case

Fig. 5. Structure of Chill-Cast Pure Brass, 83.4 Cu, 1.6 Zn. Rockwell hardness, E-56. Magnification 85 diameters.

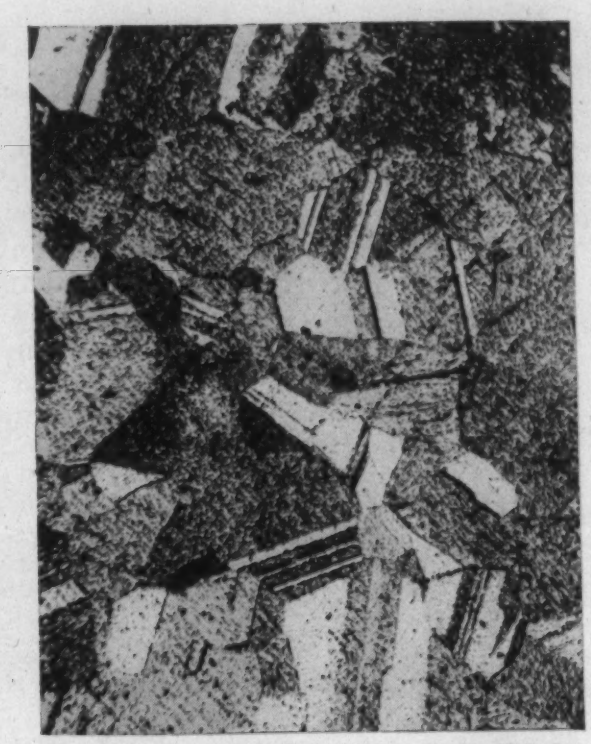


Fig. 6. Structure of Chill-Cast Alloy Brass, 82.8 Cu, 15.8 Zn and 1.4 Mg_2Si, Annealed at 700 deg. Rockwell hardness, E-45. Magnification 85 diameters.

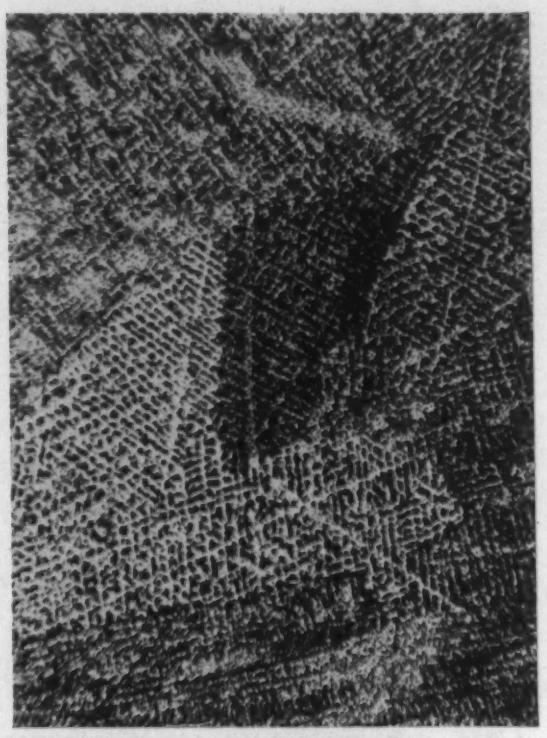


Fig. 7. Structure of Chill-Cast Alloy Brass, 83.7 Cu, 14.2 Zn, 2.0 Mg_2Si. Rockwell hardness, E-71. Magnification 85 diameters.

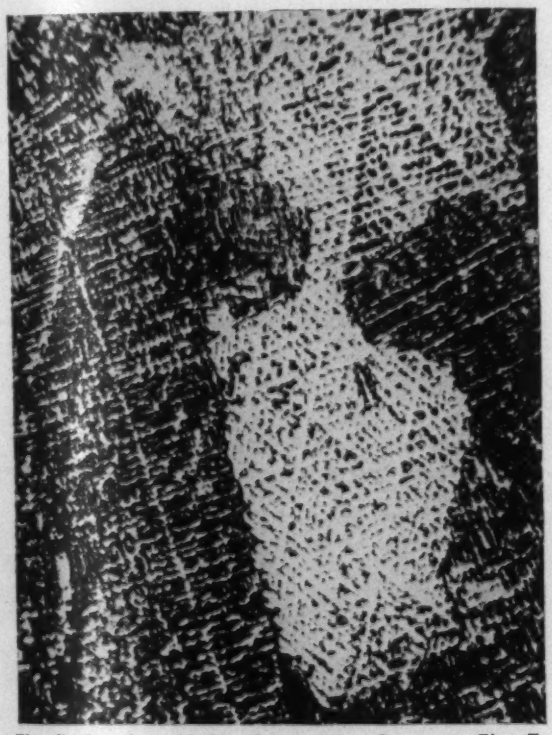


Fig. 8. Structure of the Same Alloy Brass as Fig. 7, Annealed at 450 Deg. Rockwell hardness E-79. Magnification 85 diameters.

Fig. 9. Structure of the Same Alloy Brass as Fig. 7, Annealed at 800 Deg. Rockwell hardness, E-49. Magnification 85 diameters.

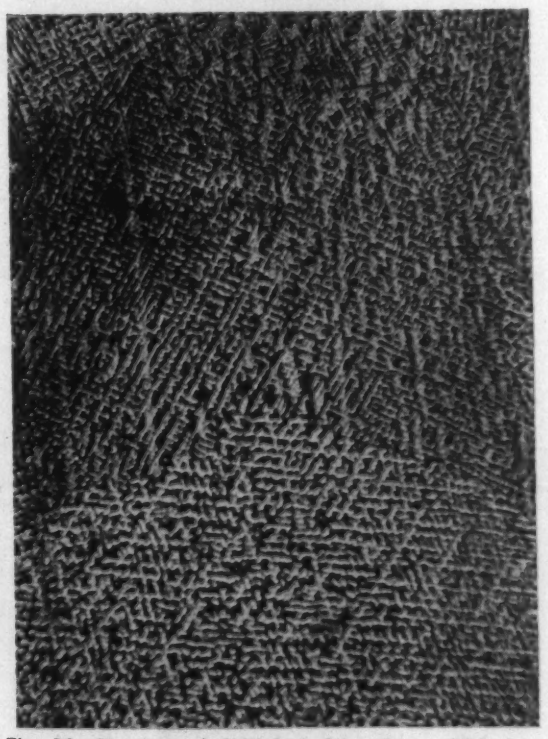


Fig. 10. Structure of Chill-Cast Alloy Brass, 83.2 Cu, 13.7 Zn, 3 Mg_2Si Rockwell hardness, E-83. Magnification 85 diameters.

Fig. 11. Structure of the Same Brass as Fig. 10, Annealed at 700 Deg. Rockwell hardness E-77. Magnification 85 diameters.

Fig. 12. Structure of Chill-Cast Alloy Brass, 81.8 Cu, 13.4 Zn, 4.7 Mg_2Si. Rockwell hardness E-99. Magnification 85 diameters.

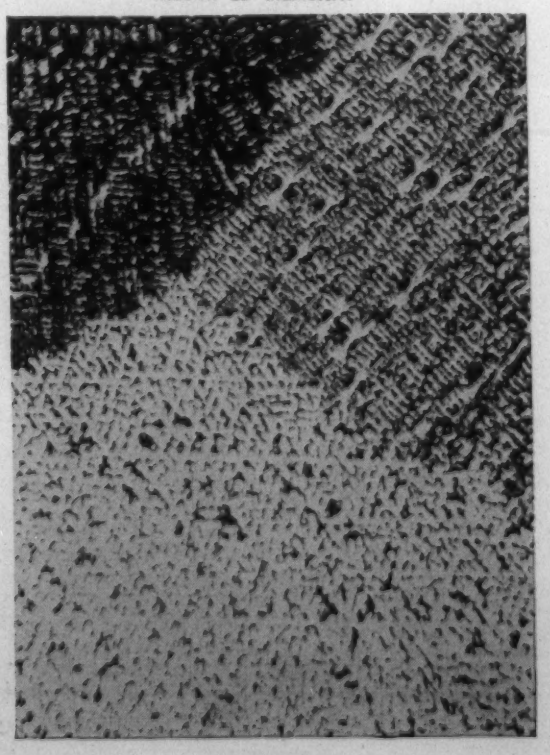


Fig. 13. Structure of the Same Brass as Fig. 12, Annealed at 700 Deg. Rockwell hardness E-97. Magnification 85 diameters.

ten or more readings were taken and averaged. Although the E scale does not extend beyond 100, a few readings in the annealed specimens fell above this number and are included as such for ease of comparison with the values below 100.

The results of the hardness determinations are recorded in the graphs of Figs. 2 and 3. It is seen

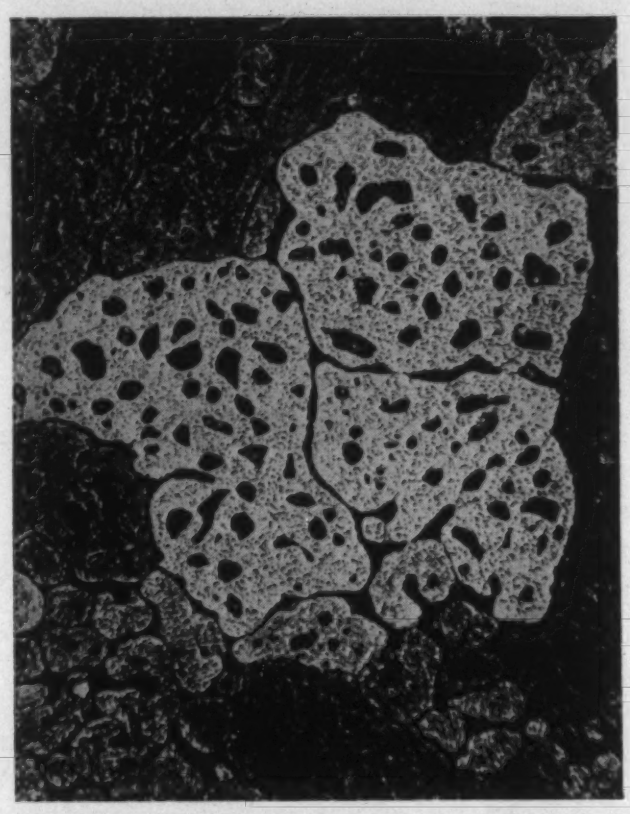


Fig. 14. Structure of the Same Brass as Fig. 12, Annealed at 800 Deg. Rockwell hardness E-91.5. Magnification 85 diameters.

(Fig. 2) that the hardness of the chill-cast samples varies almost linearly with the percentage of magnesium silicide. The effect of age-hardening at room temperature is practically nil, since no greater changes in hardness number than 1 to 1.5 were found, even after a period of 31 days. On the other hand, annealing brings about considerable changes in hardness. The time of annealing was for all temperatures 2 hrs. except for the highest temperature used (800 deg. C.) when the time was cut down to 45 min. Annealing at 175 deg. has only a slight hardening effect. As the annealing temperature is raised to 300 deg. all samples show a marked increase in hardness, except the pure brass. A rise to 450 deg. brings all the alloy brasses to their maximum hardness except sample No. 6 (4.72 per cent Mg_2Si) which attained its maximum hardness on annealing at 550 deg. Beyond this temperature the hardness drops off in all cases, least of all in sample No. 6.

The results of the annealing at 800 deg. are somewhat erratic, a slight rise for two samples (Nos. 4 and 5) being recorded (not expressed in the curves). The considerable hardness after the highest annealing for the alloy brasses as compared with the pure brass is quite noticeable. This difference comes also to the fore in Fig. 3 where the data for cold rolled and subsequently annealed samples are plotted. The rolling was carried out with small cylindrical pieces (⅜ in. in diam.) taken from the middle finger of each casting. All specimens were run through a hand-operated rolling machine. Sample No. 6 broke after one pass, at a reduction of 16.8 per cent; sample No. 5 could be reduced 28.2 per cent. Sample No. 4 was reduced in two passes to an extent of 46 per cent. The remaining alloy brasses were reduced 65 per cent in three passes while the pure brass was reduced 80 per cent. The maximum hardness after rolling varied from 100.5 for the pure brass to 108.6 for sample No. 4.

Annealing at a temperature of 450 deg. reduced the hardness for all but two samples (Nos. 5 and 6) where a slight increase was noticed. Annealing at still higher temperatures (625 and 800 deg.) causes a rapid fire drop in hardness, most pronounced for the pure brass, and least for the alloy with the greatest percentage of magnesium silicide. The extreme values (after annealing at 800 deg.) were 12.2 and 70 respectively. These values are considerably lower than for the unworked, annealed specimens (25 and 91.5 respectively).

The electrical resistance was measured with a Kelvin-double bridge on smooth cylindrical rods of 1 cm. in diameter and 12 cm. in length. In Fig. 4 the conductivity in percentage (on the basis of 100 for pure copper = 0.580 microhm^{-1} cm.$^{-1}$) is recorded for all seven samples; first, for the specimens as cast, and next after annealing for 2 hrs. at temperatures of 175, 300, 450, 550, and 700 deg. Annealing produced no change in the conductivity of pure brass while that of the alloy brasses increased somewhat up to a maximum (after annealing at 550 deg.) followed by a decrease on annealing at still higher temperatures.

Determinations of tensile strength and per cent elongation were made on small test bars of the various alloys, but proved to be inconclusive on account of the presence of flaws and blowholes in some of the specimens. The results on sound test bars indicated that the tensile strength increased with higher percentages of magnesium silicide.

With regard to the workability, it may be said that the alloy brasses sawed and drilled more freely and

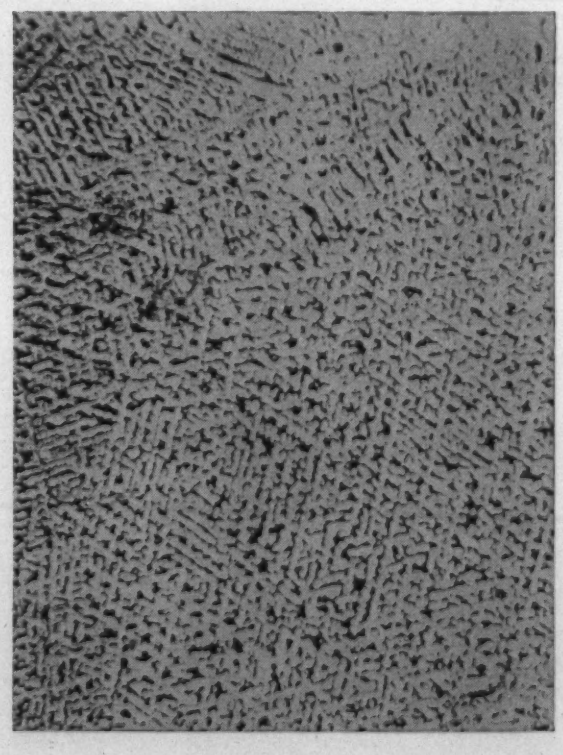


Fig. 15. Structure of the Same Brass as Fig. 12, Chill Cast, Reduced 17 Per Cent by Cold Rolling. Rockwell hardness E-105. Magnification 85 diameters.

were easier to turn down on the lathe than the pure brass. The alloy brasses, particularly the ones high in magnesium silicide, were too brittle for cold rolling. Specimen No. 3 began to peel on rolling, No. 4 split lengthwise, while samples Nos. 5 and 6 either cracked or crumbled when moderate reductions in cross sections were attempted. Only the pure brass

and the alloys with 0.66 and 1.45 per cent magnesium silicide could be reduced 70 to 80 per cent without harm to the alloy.

The thermal behavior was studied by taking cooling curves for the pure brass and for the alloys with 2.05 and 4.72 per cent magnesium silicide. The initial solidification temperature of the pure brass was found at 1020 deg., which checks with the value obtained from the copper-zinc diagram. The addition of 2 per cent magnesium silicide lowered the freezing point to about 1005 deg. while 4.7 per cent magnesium silicide decreased it to 980 deg. These

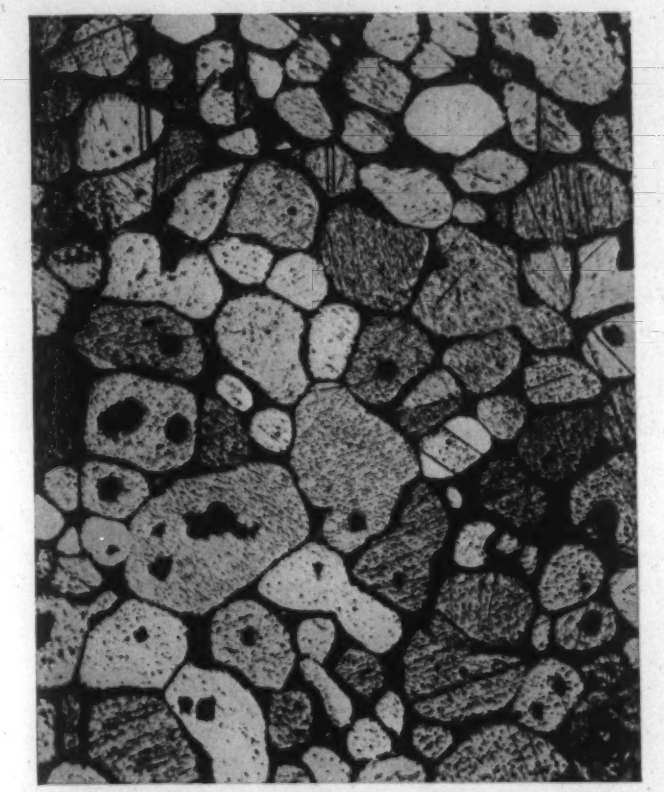


Fig. 16. Structure of the Same Brass as Fig. 12, Chill Cast, Reduced 17 Per Cent by Cold Rolling, then Annealed at 800 Deg. Rockwell hardness E-70. Magnification 85 diameters.

average values may be a trifle high because several runs had to be taken and some zinc may have been lost through volatilization and oxidation. The result indicates that we are still dealing with alpha brasses although the silicide has about twice the effect of an equal percentage of zinc in lowering the initial freezing point of brass.

All specimens were polished and afterwards etched with a solution of 50 gr. of sodium bichromate in 925 cc. of water, acidified with 25 cc. of concentrated sulphuric acid. Photomicrographs were taken of all samples, after casting, after annealing at 450, 700, and 800 deg. and also after being cold rolled, and subsequently annealed at 450, 625, and 800 deg. A comparison of the microstructures of the pure brass and of the alloy brasses both in the chill-cast and in the annealed state shows that pure brass possesses a polygonal grain structure whereas the alloy brasses present a more and more pronounced dendritic structure as the percentage of magnesium silicide increases.

This may be ascribed to the presence of magnesium silicide in solid solution which hinders the mutual diffusion of zinc and copper. These dendritic cores do not disappear completely, even on annealing at 700 deg. in samples containing 3 per cent and more magnesium silicide. After annealing at 800 deg., however, polygonal grains result, as exhibited in Figs. 14 and 16, where a separation of the silicide in the form of hard globules becomes evident. The cold rolled and annealed specimen, (Fig. 16), shows a finer grained brass with more separation of silicide along the boundaries. The resulting material is much weaker than the unworked, annealed material (Fig. 14).

Summary and Conclusions

A series of alloy brasses were prepared by adding varying amounts of magnesium silicide (up to 4.7 per cent) to a brass of approximately 85-15 composition. The effect of the added silicide was investigated by a study of the specific gravity, hardness, tensile strength, electrical conductivity, cooling curves, and microstructure.

The alloy brasses are much harder than the pure brass and show a decided increase in hardness and electrical conductivity on annealing at successively higher temperatures. Maximum hardness is reached at temperatures ranging from 450 to 550 deg.

While no age-hardening was observed, the temperature-hardening and the increase in conductivity on heating can be readily explained on the basis of the well-known theory developed by Jeffries and Archer.

The hard particles of silicide that remain scattered throughout the brass after prolonged annealing at high temperatures produce a brass that might possibly find application as bearing metal, and, generally speaking, in all cases where strength, hardness, and machinability are required.

(This article is from a thesis presented to the faculty of Rensselaer Polytechnic Institute in June, 1935, in partial fulfillment of the degree of B.S. in Chemistry.)

References

[1] *Metals & Alloys*, Vol. 1, 1929, pages 455-457, 502-507.
[2] *Journal*, Institute of Metals, Vol. 10, 1921.
[3] *Chemical & Metallurgical Engineering*, Vol. 25, 1921, page 1001.
[4] Thesis, Rensselaer Polytechnic Institute, 1931
[5] Thesis, Rensselaer Polytechnic Institute, 1934.
[6] *Zeitschrift für anorganische Chemie*, Vol. 61, 1908, page 46.
[7] *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 151, 1926, page 1.
[8] *Proceedings*, Physical Society (London), Vol. 36, 1924, page 341.

NOTCHED BAR TESTING—IV

BY S. L. HOYT

Director of Metallurgical Research, A. O. Smith Corp., Milwaukee

Concluded from the April Issue

The Mesnager Test Bar

IT APPEARS THAT the large 30 mm. bar has given satisfactory results in Germany, and likewise that the small 10 mm. Mesnager bar has been satisfactory in France and Italy. In Germany it was felt lately that a smaller and cheaper bar should be available for as much use as was feasible. This resulted in development work which was done first by two committees, one representing the users, the Deutscher Verband für die Materialprüfungen der Technik, and the other the producers, the Verein deutscher Eisenhüttenleute. These committees conducted their individual tests and then the two interests joined their efforts in a final and cooperative study which resulted in specific recommendations for a small bar. The variables of notched bar testing, which have been discussed here, were understood and taken into account both in the exploratory work and in arriving at the final choice.

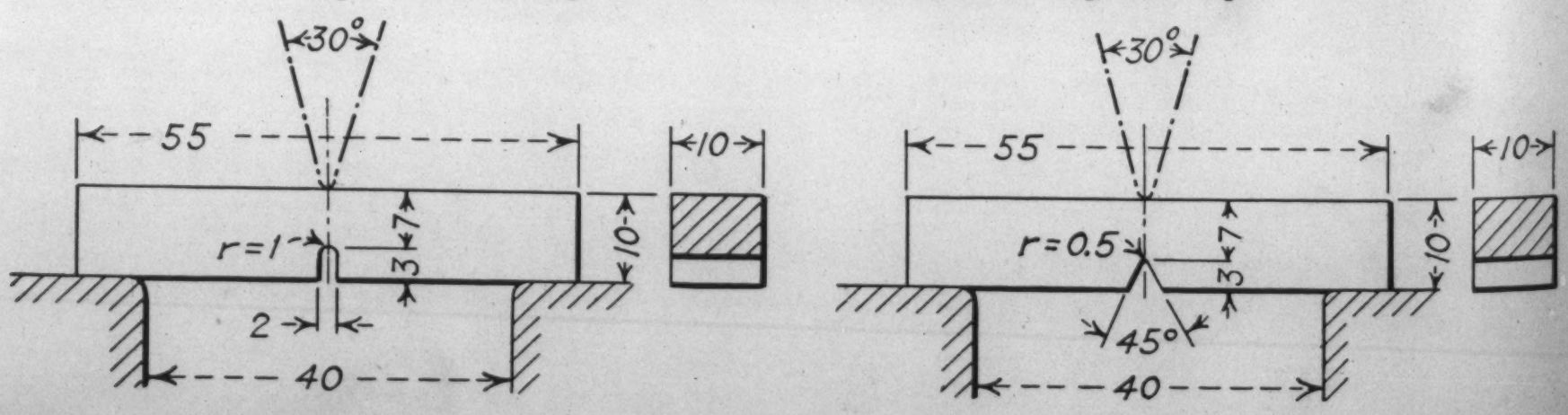
The German engineers took the stand that a modified Mesnager test bar, broken at the common laboratory temperature, was nearly the equivalent of the large 30 mm. bar and would be satisfactory for most test purposes. The bar of their choice is shown in Fig. 8 so that the only departure from the Mesnager bar is the depth of the notch which is 3 mm. instead of 2 mm. The design of the notch was held to give a sufficiently pronounced notch effect to avoid the necessity for breaking two different bars, while it was also held impractical to use two different test temperatures or striking velocities. The committee also realized that their standard bar was not suited to the testing of the tougher steels. Instead of simply stepping up the test requirement and using the same bar, it recommended the use of the second bar of Fig. 8 with the sharp V notch. At the time that a report of this work was made to the New International Association for Testing Materials in 1931, only boiler plate and steel castings were still tested with the 30 mm. bar[17].

A second large scale study of notched bar testing of recent years is that of Italian engineers who adopted the French Mesnager bar with 2 mm. notch for the control of purchases of railway materials, and later of other steel requirements. The Germans had pointed out that the depth of the notch must exceed a certain minimum to develop the full effect. Shallower notches came in that range over which the impact value varied too greatly with depth and were not as sensitive for the detection of more pronounced cases of notch brittleness. The Italians, on the other hand, pointed to the years of use of the 2 mm. notch in France and took the position that their notch was equally as sensitive as the 3 mm. notch, though without refuting the German evidence. Later Giolitti reported that subsequent work had confirmed the Italian position on the 2 mm. notch and had even shown the shallower notch to be more sensitive than the 3 mm. notch[18]. No reasons were advanced as to why that should be so, and there the matter stands. The situation is not conducive to the establishment of an international standard; and the English have a still different type of notch which they would not readily give up. In this country the whole question has never received the critical attention that is involved in setting up a standard test.

The Utility of the Notched Bar Test

The utility of an acceptance test depends on reliable correlations between test results and service behavior, or upon the ability of the test to detect material which either would or would not meet the service requirements. The tensile test supplies such information with respect to strength and its long and enviable record has but few instances in which parts have failed due to lack of strength. The notched bar test has to do with quite different factors and comes much closer to more common causes of failure. In making this statement I do so with the interpretation that the notch effect is broader than the stress concentration which occurs at the base of the notch. In practice we may say that the notch effect is a stress condition which accentuates the tendency of ductile metals to fail by cleavage rather than to deform. Thus it appears that, paradoxically enough, a part can fail even though it be strong enough, because it lacks notch toughness. By that I mean that material of the same strength does not fail when possessing the toughness required by that particu-

Fig. 8. German Mesnager Bar (Left). German Substitute Bar for Tough Steels (Right).



lar service. Furthermore, the correct solution of these failures is not to increase the size of the part but to use material of adequate notch toughness. This characteristic of notch toughness, or conversely the characteristic of notch sensitivity, is closely correlated in varying degrees with a number of conditions of steel. We might say that the utility of the notched bar test lies in its unique ability to detect and evaluate the effects which these conditions have on the integrity of steel products.

I am listing below a number of conditions in steel which relate to brittleness of the type under consideration. A few of these can be controlled by microscopic examination, and some by macroscopic methods, but all are subject to definite control by the notched bar test. Many of these conditions would completely escape detection by microscopic examination or by the usual tensile tests.

1. Overheated condition from forging.
2. Overheated or poor condition from heat treating.
3. Casting structure.
4. Low temperature brittleness.
5. Temper brittleness in heat-treated steels.
6. Ageing embrittlement in mild steel.
7. Phosphorus, oxygen embrittlement, etc.
8. Segregations.
9. Laminations.
10. Coarse slag or foreign inclusions.
11. "Condition" of steel as affected by melting, refining, and deoxidation practice.

It is well recognized that brittleness can be caused by any one of the above conditions, or by combinations thereof. I believe a metallurgist would try to avoid them, though he never used the notched bar test. In fact the metallurgist who does not use the test will avoid such conditions in his important parts just as conscientiously as the one who does, and with a little luck he might have about equal success. The utility of the test is that it provides the positive control that an important step in a manufacturing process should have and gives a check on these somewhat intangible quality factors. Points 3 and 5 are particularly useful in this connection for a raw steel casting and a temper brittle steel forging are perfectly strong and ductile in the tensile test. It is their insidious weakness in general service that makes one use corrective heat treatment.

We have said nothing about service which involves a notched condition. While the notched bar test is particularly suited to selecting material for such service, it is by no means limited to such use. Testimony like the following serves to illustrate the breadth of the utility of the test. "From seven years experience in Charpy testing of SAE 1045 steel, running above 1000 mill heats, and from several different mills, it has been definitely determined that good Charpy characteristics at 600 and 800 deg. F. tempering temperatures prevent service failures in tractor parts."[19] This is quoted from Mr. Riegel who, as metallurgist for the Caterpillar Tractor Co., has had to guard steel "quality" for parts which must stand exacting service.

How difficult it would be to predict the stress conditions of these parts in service! I might also cite the case of the Russian "catastrophe winter" whose records correlated extra heavy rail breakage with low notch toughness. In many types of service one cannot foresee what types of stress conditions or stress concentrations will be met; the peculiar stress condition of the notch effect which leads to the cleavage fracture may come from without or, as in case of rails with transverse fissures, it may rise internally. The safe guide for important applications is the enlightened use of the notched bar test.

One metallurgical friend of mine carries the Charpy test a step further. He uses a Brinell test and a few Charpy bars to control the quality of forgings. With the chemical composition known and with a fixed schedule of mechanical and heat treatments, the hardness shows if the treatments were properly carried out for strength, etc., while the Charpy test shows if the quality is satisfactory.

I am going to cite an experience which illustrates the utility of the notched bar test and also brings up the question of view point again. Considerable difficulty was being experienced with certain parts which were made of a high grade but relatively new steel. After going into the situation it became clear that I had an opportunity to do some scientific sleuthing. My clues were: Brittle failure, ductility in the tensile test, a steel whose metallurgical behavior was not very well known, a heat treatment which was an oil quench and a fairly high draw. We might put alongside of this the old line of reasoning which would be about as follows: High grade steel, well controlled heat treatment, good inspection, perfect tensile properties, the part broke, and hence it should be made bigger. I asked to have one Charpy bar quenched from the draw and another slowly cooled as usual. The test showed, what was new at the time, that this steel was subject to temper brittleness. After finding that out, the solution was easy while the point of view was not clouded by misconceptions of the effect of "shock."

Another experience of a different kind may also be worth while citing. A structure was made of a steel that is sensitive to over heating, though this sensitivity is not reflected in the tensile test. This structure was given what was presumably a very severe set of tests which included terrific blows of sufficient strength to make large dents but without showing up any weakness. The metal was strong and ductile, which fully confirmed the results of the tensile tests made on coupons. Out of curiosity I broke some Charpy bars of this steel and found that it had an extremely low impact value, the metal was definitely notch brittle and would have been treacherous in any type of service which produced the stress conditions of the notch effect. If one had the preconception that the impacts of the large scale test should correlate with the Charpy test on notched bars, this experience would go a long way towards making him feel that the Charpy test meant nothing. Of course the Charpy test does not necessarily correlate with either tests or service conditions which do not involve the notch effect. By the same token this structure, though made of steel that was in an extremely notch brittle condition, might very well have a long and useful life in service and, if it failed from some unhappy circumstance, it could show a perfectly normal ductile behavior. There need be no mystery about a fully brittle material standing up under shock or about a notch sensitive material which deforms under heavy blows and, I might add, about a normally ductile material which fails in service as though it were brittle. In brief while the tensile test of a necking material furnishes proper criteria for behavior which likewise involves deformation and a fibrous fracture, if the cleavage strength lies too low for the resistance to deformation, the tensile test on plain bars can furnish no adequate criteria, that is the province of the notched bar test.

Uniformity of Results

In testing materials one becomes accustomed to uniformity in test results with good checks from similar samples and even from consecutive heats of steel which are to be used for the same application. These results are also predictable with reasonable accuracy from the chemical analysis and the treatments through which the material passes. This situation is different with the notched bar test. While the results are usually in satisfactory agreement one may and frequently does get quite wide variations. Upon noting the variation in results of the notched bar test and comparing with the uniform chemical analyses and tensile test results, one may draw different conclusions, depending on his previous experience and on the basis of his interpretation. Does this lack of agreement reflect vagaries of the test itself, or does it reveal actual variations in the material? This situation creates a hazard for the acceptance and use of the notched bar test and deserves serious attention.

There are three major questions which must be answered: (1) the first relates to disagreement among results of check tests from the same part, though the tensile properties agree, (2) the second relates to variations from heat to heat, though the tensile results agree, and (3) the third relates to poor impact values, though the tensile results indicate no impairment in quality.

With respect to the first, one frequently hears that the results are unreliable, by which is meant that, due to imperfections in the testing procedure, sometimes high results and sometimes low results will be secured from identical samples. The chance causes of the spread are assigned to the test procedure and not to the material itself. Charpy appreciated the situation which was created by experience such as this and, with Cornu-Thenard, made a special study of uniformity of test results from a block of steel which they had reason to believe was chemically and physically homogeneous. They report impact figures which agree among themselves as close as 1 to 2 per cent and which scarcely ever disagreed by as much as 4 per cent[20]. This agreement is as close as can be claimed for tensile properties and is so good that one can no longer raise serious objection on the score that the test *cannot* give good check results. Upon engaging in the development of the test at Schenectady, it occurred to me that methods of routine testing might lead to a larger spread of results, unless one were willing to resort to expensive machine shop operations. This led to a check of the results of Charpy and Cornu-Thenard by methods which were to be used to cheapen the cost of making the test bars. With test bars which were machined no closer than ± 0.002 in., a nicely made nickel steel gave very satisfactory checks of the order of a few foot pounds. I could no longer ascribe real variations in test results to vagaries of the test and I believe the point is now seldom raised any more. The logical explanation of variations in duplicate samples is that the greater sensitivity of the notched bar test to factors which are glossed over by the tensile test, or missed entirely, bring out differences which are very real. On the other hand we dare not ascribe all such variations to one cause or to the same type of cause. Many steels show sudden and marked change of behavior with changes in test temperature, velocity of impact, and in width of bar for a given notch. If the particular test conditions coincide with the critical values of these variables for the material being tested, we may get a natural spread in results. Small variations in the material are magnified tremendously under such circumstances. Aside from such causes of a spread in results it is possible to get variations which are due to segregations, laminations, coarse foreign inclusions, etc. In technical practice it would be highly desirable to differentiate between chance and controllable causes of these variations, and that could be done by suitable analytical methods.

Having answered the first question there is not much to be said about variations from heat to heat of steel. The notched bar test is sensitive to manufacturing conditions and they are rather vividly brought to light by this test. They may or may not be significant, depending on the use of the material.

The third question has already been rather fully dealt with and there is no doubt that the tensile test completely misses serious cases of brittleness which are clearly and unequivocally shown by the notched bar test. The tensile test is a static test and therefore does not bring out brittleness or lowered ductility which may develop when the material is rapidly strained. The tensile test is a test of a plain bar and its results can be used to predict behavior only in case the stress system there encountered produces the same type of deformation.

Concluding Remarks

IN this paper I have attempted to clarify notched bar testing by distinguishing between it and impact testing and by showing how the notch acts and what peculiarities of metallic behavior it brings out. The principal feature here was shown to be the newly discovered property of the cleavage strength of the undeformed metal. Methods of testing and the interpretation of the test results have been discussed, while the theory of notch behavior has been given in enough detail to bring support to the ideas advanced. In this way the discussion of the test places emphasis on its technological character, a feature that must dominate both the test procedures and the use of the test results. The utility of the test was shown to lie in its unique ability to detect harmful conditions in steel and eleven examples are listed which may be encountered in technical practice, individually or collectively. Perhaps the principal use of the test is for controlling the heat treatment of steel and to check that inherent "quality" which results from the methods and materials employed in the manufacture of the steel. While the result of the test is given a quantitative evaluation in terms of the energy absorbed in a standard test, one should interpret the results of a given test for a specific application as "satisfactory" or "unsatisfactory" with a clear conception of the meaning of the test used, of the characteristics of the steel being tested, and of the service requirements.

After all, any metal can be made to fail with a brittle fracture and low energy absorption. Of even greater significance than the actual impact value are the conditions which are required to produce the brittle type of failure.

References (Concluded)

[17] M. Moser. New International Association of Testing Materials, Zurich, 1931, Group A; *Transactions*, American Society of Mechanical Engineers, Applied Mechanics, Vol. 1, July-Sept., 1933, page 105.

[18] F. Giolitti. *Metal Progress*, Vol. 27, Jan. 1935, page 45.

[19] G. C. Riegel. *Transactions*, American Society for Metals, Vol. 22, 1934, page 1167.

[20] G. Charpy and A. Cornu-Theward. *Journal*, Iron and Steel Institute, Vol. II, 1917, page 61.